SEPTEMBER 15, 1939 PHYSICAL REVIEW VOLUME 56

Theory of Secondary Emission

D. E. Wooldridge
Bell Telephone Laboratories, New York, New York

(Received June 9, 1939)

The production of secondary emission by the interaction of bombarding electrons with the valence electrons of a metal target is quantum-mechanically treated. When the results are modified by considerations having to do with the relative rates of absorption of the primary and secondary particles, yield-*vs.*-bombarding energy curves are obtained which approximate the results of experiment. The primary voltage required for maximum yield, the effect of work function on the emission, and the energy range of the secondary particles are semi-quantitatively derived in terms of the properties of the target material.

IN Fröhlich's[1] theory of secondary emission there are errors which seriously affect the nature of the conclusions reached.[2] When these errors are removed, the result is a prediction that the rate of production of secondaries is independent of the energy of the bombarding primaries, rather than proportional to the square root of this energy, as Fröhlich concluded. But such a result does not appear to resemble the results of measurements. It develops that the shape of the secondary yield *vs.* primary energy curve may be a result of the fact that, in a distance less than the mean free path of the secondaries, the primary electrons may lose so much energy that they can produce no more secondaries. This conclusion will be reached as one of the products of the theory of secondary emission which is developed in the following pages.

At the beginning of Fröhlich's treatment, certain assumptions are made as to the nature of the fields inside the metal, which effectively make the theory a one-dimensional one. For example, one could not obtain any information about the distribution in direction of the secondaries from a theory of this sort. Furthermore, these assumptions make it impossible to estimate the relative importance of the neglected terms in the final result. In this paper a development is presented in which these assumptions are not made. It has been found possible to set up the quantum-mechanical problem in such a way as to lead to a solution which is more general than that given by Fröhlich.

For the convenience of the reader, this paper is divided into two sections. In the first section the fundamental problem of the interaction between the primary and the metal electrons is treated quantum-mechanically. In the second section the results of this quantum-mechanical treatment are so manipulated as to lead to explicit conclusions concerning the nature of secondary emission which can be compared with experiment.

I. Quantum-Mechanical Development

The general nature of the problem has been stated by Fröhlich and may be repeated here very simply. A beam of electrons is caused to bombard a metal target. After penetrating the surface, these "primary" electrons move in a region in which they must occasionally approach some of the valence (or "lattice") electrons which are thought of as traveling around in the metal. Because of the repulsive forces thus set up, some of the lattice electrons may be given high enough energies that they can escape from the target and be observed as "secondary" electrons. In treating any problem of this nature one generally commences by neglecting the fields in the metal. But, as Fröhlich has pointed out, the usual type of secondary emission, in which electrons are ejected from the bombarded surface of the target, cannot be accounted for by this "free electron" approximation. Obviously, energy and momentum could not be conserved. Hence

---

[1] H. Fröhlich, Ann. d. Physik 5, **13**, 229 (1932).

[2] For example, in the equation at the top of p. 240 of Fröhlich's paper, the important term $-K_x(\pm k_x+2\pi n/a)$ has been omitted. In addition, the integration of Eq. (19″), p. 238, through which Fröhlich concluded that the secondary yield should reach a maximum and then decrease with increasing primary energy, has been extended into a region of values which can be shown to be excluded by conservation of energy considerations.

it is necessary for the theory to take account of the fact that the valence electrons are not free, but are acted upon by forces which make it possible for them to "bounce" out of the bombarded surface, the net momentum change of the process being absorbed by the metal lattice.

Although it is necessary to take into account the binding of the valence electrons to the lattice, it is nevertheless a good approximation to neglect binding terms as far as the primary electrons are concerned—for we are interested only in the forces exerted by the primary electrons and these forces will not be greatly influenced by the small restraints acting on the primaries.

The problem will then be set up as follows. Initially a beam of primary electrons, each of kinetic energy $\hbar^2K^2/2m$ and of momentum $\hbar\mathbf{K}$, is traveling through the metal lattice. Inside the lattice there is a single electron, which initially occupies one of the quantum states permitted by the particular periodicity of the lattice fields. Because of the interaction between these two electrons, there is a calculable rate at which the initial state, as above defined, varies into other states, some of which lead to secondary emission. It is this rate of change which is to be computed.

In this computation the "primary" and "lattice" or "metal" electrons (as in Fröhlich's development) will be treated like distinguishable particles. The exclusion principle will finally be taken account of in two ways—first, by the use of Fermi statistics in summing the results of the above-outlined calculations over all the lattice electrons; second, by ruling out all transitions which leave an electron in an already occupied state.

The lattice will be assumed to have a simple cubic structure throughout this calculation. It will be shown that the results obtained can be applied to other crystalline types without serious error, however. In a simple cubic lattice, the unperturbed eigenfunctions[3] are of the form given by Bloch

$$u_{\mathbf{k}}(\mathbf{r})\exp[i(\mathbf{k}\cdot\mathbf{r})],$$

where $u_{\mathbf{k}}(\mathbf{r})$ has the periodicity of the lattice. For most metals $u_{\mathbf{k}}(\mathbf{r})$ differs only slightly from unity ($\mathbf{k}$ is *not* the "reduced" wave vector) so that $\hbar\mathbf{k}$ is very nearly the momentum of the electron and $\hbar^2k^2/2m$ is very nearly its kinetic energy. As the unperturbed probability amplitude of our system of two particles we take

$$\psi_{\mathbf{k},\,\mathbf{K}}=\frac{1}{\Omega}u_{\mathbf{k}}(\mathbf{r})\exp[i(\mathbf{K}\cdot\mathbf{R})+i(\mathbf{k}\cdot\mathbf{r})],$$

where, of course, $\psi\psi^*d\tau_{\mathbf{R}}d\tau_{\mathbf{r}}$ is the probability of finding a primary electron in the volume element $d\tau_{\mathbf{R}}=dXdYdZ$ at the position $\mathbf{R}$ and a lattice electron in the volume element $d\tau_{\mathbf{r}}=dxdydz$ at the position $\mathbf{r}$. ψ has here been normalized so as to require the existence of one primary electron and one lattice electron somewhere within the volume Ω, and $u_{\mathbf{k}}$ is assumed to have been normalized so that

$$(u_{\mathbf{k}}^*u_{\mathbf{k}})_{\mathrm{Av}}=1. \tag{1}$$

For this problem the perturbation potential is simply the Coulombian repulsion energy

$$U=e^2/|\mathbf{R}-\mathbf{r}|.$$

From the usual treatment of the method of variation of constants[4] we can write

$$|a_{\mathbf{k}',\,\mathbf{K}'}|^2=\frac{1}{\hbar^2}|U_{\mathbf{k},\,\mathbf{K};\,\mathbf{k}',\,\mathbf{K}'}|^2\cdot\frac{2(1-\cos\epsilon t)}{\epsilon^2}, \tag{2}$$

where

$$U_{\mathbf{k},\,\mathbf{K};\,\mathbf{k}',\,\mathbf{K}'}\equiv\frac{1}{\Omega^2}\int\frac{e^2}{|\mathbf{R}-\mathbf{r}|}u_{\mathbf{k}}(\mathbf{r})u_{\mathbf{k}'}^*(\mathbf{r})\times\exp[i(\mathbf{K}-\mathbf{K}')\cdot\mathbf{R}+i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}]d\tau_{\mathbf{r}}d\tau_{\mathbf{R}}$$

and

$$\epsilon\equiv(E_{\mathbf{k}',\,\mathbf{K}'}-E_{\mathbf{k},\,\mathbf{K}})/\hbar. \tag{3}$$

In the usual way $|a_{\mathbf{k}',\,\mathbf{K}'}|^2$ is interpreted as representing the probability that, at the time t, the system will be in the state specified by the vectors $\mathbf{k}'$ and $\mathbf{K}'$ when, at $t=0$, the system was started in the state $\mathbf{k},\mathbf{K}$. As Fröhlich has pointed out, the restrictions imposed by the Born approximation can be shown to be unimportant down to primary energies lower than those with which we shall be concerned.

In evaluating $U_{\mathbf{k},\,\mathbf{K};\,\mathbf{k}',\,\mathbf{K}'}$ we can employ a

---

[3] N. F. Mott and H. Jones, *Properties of Metals and Alloys* (Oxford, 1936), p. 57.

[4] Reference 3, p. 250.

result given by Bethe,[5] who showed that

$$\int \frac{\exp\,[i(\mathbf{K}-\mathbf{K}')\cdot\mathbf{R}]}{|\mathbf{R}-\mathbf{r}|}d\tau_{\mathbf{R}}=\frac{4\pi\exp\,[i(\mathbf{K}-\mathbf{K}')\cdot\mathbf{r}]}{|\mathbf{K}-\mathbf{K}'|^2}. \tag{4}$$

Hence

$$U_{\mathbf{k},\,\mathbf{K};\,\mathbf{k}',\,\mathbf{K}'}=\frac{1}{\Omega^2}\cdot\frac{4\pi e^2}{S^2}\int u_{\mathbf{k}}(\mathbf{r})u_{\mathbf{k}'}^*(\mathbf{r}) \times\exp\,(i\mathbf{S}\cdot\mathbf{r}+i\mathbf{s}\cdot\mathbf{r})d\tau_{\mathbf{r}}, \tag{5}$$

where

$$\mathbf{S}\equiv\mathbf{K}-\mathbf{K}';\qquad \mathbf{s}\equiv\mathbf{k}-\mathbf{k}'.$$

We may expand

$$u_{\mathbf{k}}(\mathbf{r})=\sum_{\mathbf{m}}a_{\mathbf{m}}(\mathbf{k})\exp\,[2\pi i(\mathbf{m}\cdot\mathbf{r})/a].$$

"a" is the lattice spacing and **m** is a vector for which each component is a positive or negative integer. The summation extends over all values of **m** which this single restriction permits. The normalization condition (1) requires that

$$\sum_{\mathbf{m}}a_{\mathbf{m}}a_{\mathbf{m}}^*=1.$$

With the above expansion, Eq. (5) becomes

$$U_{\mathbf{k},\,\mathbf{K};\,\mathbf{k}',\,\mathbf{K}'}=\frac{1}{\Omega^2}\frac{4\pi e^2}{S^2}\sum_{\mathbf{m},\,\mathbf{n}}\int a_{\mathbf{m}}(\mathbf{k})a_{\mathbf{n}}^*(\mathbf{k}') \times\exp\,[i(\mathbf{S}+\mathbf{s}+2\pi\boldsymbol{\varrho}_{mn}/a)\cdot\mathbf{r}]d\tau_{\mathbf{r}},$$

where

$$\boldsymbol{\varrho}_{mn}\equiv\mathbf{m}-\mathbf{n}.$$

This may also be expressed as

$$U_{\mathbf{k},\,\mathbf{K};\,\mathbf{k}',\,\mathbf{K}'}=\frac{1}{\Omega^2}\frac{4\pi e^2}{S^2}\sum_{\rho}\Big(\big[\sum_{\mathbf{m}}a_{\rho+\mathbf{m}}(\mathbf{k})a_{\mathbf{m}}^*(\mathbf{k}')\big] \times\int\exp\,[i(\mathbf{S}+\mathbf{s}+2\pi\boldsymbol{\varrho}/a)\cdot\mathbf{r}]d\tau_{\mathbf{r}}\Big), \tag{6}$$

where $\boldsymbol{\varrho}$ and **m** are to be summed independently over all vectors which have integral components.

At this point we may notice that, for $U_{\mathbf{k},\,\mathbf{K};\,\mathbf{k}',\,\mathbf{K}'}$ to have an appreciable value,

$$\mathbf{S}+\mathbf{s}+2\pi\boldsymbol{\varrho}/a\sim 0. \tag{7}$$

This is our momentum principle. In the special case of free electrons only the term $\boldsymbol{\varrho}=0,0,0$ appears in the summation and (7) reduces to the familiar conservation of momentum relation.

From (6), Eq. (2) may now be written

$$|a_{\mathbf{k}',\,\mathbf{K}'}|^2=\frac{1}{\hbar^2}\frac{1}{\Omega^4}\left(\frac{4\pi e^2}{S^2}\right)^2\left|\sum_{\rho}\Big(\big[\sum_{\mathbf{m}}a_{\rho+\mathbf{m}}(\mathbf{k})a_{\mathbf{m}}^*(\mathbf{k}')\big] \times\int\exp\,[i(\mathbf{S}+\mathbf{s}+2\pi\boldsymbol{\varrho}/a)\cdot\mathbf{r}]d\tau_{\mathbf{r}}\Big)\right|^2 \times\frac{2t^2(1-\cos\epsilon t)}{(\epsilon t)^2}. \tag{8}$$

This expression involves the product of two terms, one of which differs from zero only when, for some allowed $\boldsymbol{\varrho}$, $\mathbf{S}+\mathbf{s}+2\pi\boldsymbol{\varrho}/a\sim 0$, the other of which is appreciable only when $\epsilon t=(t/\hbar)(E_{\mathbf{k}',\,\mathbf{K}'}-E_{\mathbf{k},\,\mathbf{K}})\sim 0$. These two conditions define regions in six-dimensional $\mathbf{k}'$, $\mathbf{K}'$ space within which $|a_{\mathbf{k}',\,\mathbf{K}'}|^2$ differs appreciably from zero. Suppose we fix $\mathbf{k}'$. Then there will be discrete values of $\mathbf{K}'$ (one for each possible value of $\boldsymbol{\varrho}$) for which the integral in (8) will have an appreciable value. For any one of these allowable values of $\mathbf{K}'$, the function $(1-\cos\epsilon t)/(\epsilon t)^2$ may or may not differ appreciably from zero. If Ω is very large, then the range of $\mathbf{K}'$ around any allowed value for which the integral in (8) is of importance will be so small that $(1-\cos\epsilon t)/(\epsilon t)^2$ may be considered constant over this region. If $\mathbf{K}'_{\rho}$ is a value of $\mathbf{K}'$, for a given **k**, **K** and $\mathbf{k}'$, allowed by our momentum principle, we obtain, by integrating (8)

$$|a_{\mathbf{k}',\,\mathbf{K}'_{\rho}}|^2=\frac{1}{\Omega^2}\cdot\frac{16\pi^2e^4}{\hbar^2}\frac{1}{S_{\rho}^4} \times\big|\sum_{\mathbf{m}}a_{\rho+\mathbf{m}}(\mathbf{k})a_{\mathbf{m}}^*(\mathbf{k}')\big|^2t^2F(\epsilon_{\rho}t)$$

where we have defined

$$F(\epsilon_{\rho}t)=\frac{2(1-\cos\epsilon_{\rho}t)}{(\epsilon_{\rho}t)^2}. \tag{9}$$

Adding such results for all possible $\boldsymbol{\varrho}$, we get

$$|a_{\mathbf{k}'}|^2\equiv\sum_{\rho}|a_{\mathbf{k}',\,\mathbf{K}'_{\rho}}|^2=\frac{1}{\Omega^2}\frac{16\pi^2e^4}{\hbar^2}t^2 \times\sum_{\rho}\Big(\frac{1}{S_{\rho}^4}F(\epsilon_{\rho}t)\,\big|\sum_{\mathbf{m}}a_{\rho+\mathbf{m}}(\mathbf{k})a_{\mathbf{m}}^*(\mathbf{k}')\big|^2\Big)$$

---

[5] H. Bethe, Ann. d. Physik 5, 5, 325 (1930).

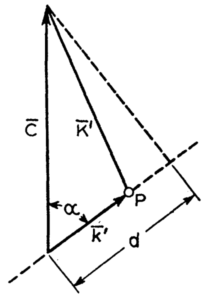

FIG. 1. Vector diagram illustrating momentum principle $\mathbf{C}=\mathbf{k}+\mathbf{K}+2\pi\boldsymbol{\varrho}/a$.

$|a_{\mathbf{k}'}|^2$ is to be interpreted as the probability, that, at the time t, a lattice electron will be found in the state $\mathbf{k}'$. In the usual way[6] the summation can be converted to an integral by multiplication by $\Omega/8\pi^3$. This gives, for the number of lattice electrons which, at time t, have their wave vectors in a range $d\tau_{\mathbf{k}'}$ around $\mathbf{k}'$,

$$dN=\frac{\Omega}{8\pi^3}\cdot\frac{1}{\Omega^2}\,\frac{16\pi^2e^4}{\hbar^2}t^2$$
$$\times\sum_{\rho}\left(\frac{1}{{S_\rho}^4}F(\epsilon_\rho t)\,\Big|\sum_{\mathbf{m}}a_{\rho+\mathbf{m}}(\mathbf{k})a_{\mathbf{m}}{}^*(\mathbf{k}')\Big|^2\right)d\tau_{\mathbf{k}'}. \quad (10)$$

This result was derived for the case wherein Ω contained only one primary and one lattice electron. Let N_p and $N_l(\mathbf{k})$ represent the actual numbers of primary and lattice electrons, respectively, present in the volume Ω, and let ρ_p and $\rho_l(\mathbf{k})$ denote N_p/Ω and $N_l(\mathbf{k})/\Omega$. If the primary current density is J_p (electrons cm^{-2} sec.$^{-1}$) and if the velocity of the primary electrons is V, then

$$\rho_p=J_p/V.$$

But $$V=\hbar K/m; \quad (11)$$

$$\therefore \quad \rho_p=J_pm/K\hbar.$$

When Eq. (10) is multiplied by $N_l=\rho_l\Omega$ and by $N_p=J_pm\Omega/K\hbar$, it becomes

$$dN=\sum_{\rho}dN_\rho,$$

where

$$dN_\rho=J_p\Omega t^2\cdot\frac{2me^4}{\pi\hbar^3}\rho_l(\mathbf{k})\frac{1}{K}\left(\frac{1}{{S_\rho}^4}F(\epsilon_\rho t)\right.$$
$$\left.\times\Big|\sum_{\mathbf{m}}a_{\rho+\mathbf{m}}(\mathbf{k})a_{\mathbf{m}}{}^*(\mathbf{k}')\Big|^2\right)d\tau_{\mathbf{k}'}. \quad (12)$$

Thus the problem reduces to a consideration of dN_ρ, for a given value of $\boldsymbol{\varrho}$. The following considerations will apply to such a case—where $\boldsymbol{\varrho}$ is fixed. Under these circumstances the momentum condition (7) has shown that the only final states which can appear are those for which

$$\mathbf{S}+\mathbf{s}+2\pi\boldsymbol{\varrho}/a=0$$

or $$\mathbf{K}'+\mathbf{k}'=\mathbf{K}+\mathbf{k}+2\pi\boldsymbol{\varrho}/a. \quad (13)$$

Let us now see what additional restrictions are imposed by virtue of the fact that $F(\epsilon_\rho t)$, in (12), has appreciable values only in the vicinity of $\epsilon_\rho=0$. This, of course, is the "conservation of energy" principle. We will assume that t is sufficiently large that $F(\epsilon_\rho t)$ is a much more rapidly varying function than any others remaining in the problem. Now for energy considerations, it is a good enough approximation to write

$$E_{\mathbf{k},\,\mathbf{K}}=\hbar^2(k^2+K^2)/2m.$$

The condition $\epsilon_\rho=0$ then becomes, simply,

$$k'^2+K'^2=k^2+K^2. \quad (14)$$

The values of $\mathbf{k}'$, $\mathbf{K}'$ which correspond to final states are those which simultaneously satisfy Eqs. (13) and (14). In Fig. 1 the vector diagram corresponding to Eq. (13) is shown. In terms of the distances and angles shown in this figure, it is easy to demonstrate that, for a given α (always measured so as to be $<\pi/2$), Eq. (14) is satisfied only by the two magnitudes of k' given by the equation

$$k'=\frac{d}{2}\left[1\pm\left(1-\frac{D^2}{d^2}\right)^{\frac{1}{2}}\right], \quad (15)$$

where it has been convenient to define

$$\mathbf{C}\equiv\mathbf{K}+\mathbf{k}+2\pi\boldsymbol{\varrho}/a \quad (16)$$

and $$D^2\equiv2(C^2-k^2-K^2). \quad (17)$$

Evidently, from Fig. 1,

$$d=C\cos\alpha.$$

In Eq. (15), k' is considered positive if its direction makes an angle of $<\pi/2$ with that of $\mathbf{C}$, negative otherwise.

The result given by Eq. (15) may be expressed in a convenient geometrical way. If a sphere of radius

$$R=[\tfrac{1}{4}(C^2-D^2)]^{\frac{1}{2}} \quad (18)$$

---

[6] Reference 3, p. 56.

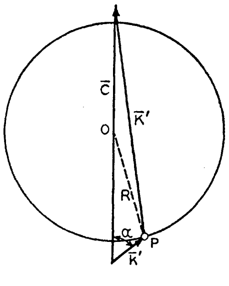

FIG. 2. Diagram illustrating effect of simultaneous operation of momentum and energy principles. The only probable transitions are those for which P lies on the sphere of radius

$$R=\tfrac{1}{2}[K^2-2\mathbf{K}\cdot(\mathbf{k}+2\pi\boldsymbol{\varrho}/a)+k^2-(2\pi\boldsymbol{\varrho}/a)^2-2\mathbf{k}\cdot(2\pi\boldsymbol{\varrho}/a)]^{\frac{1}{2}}.$$

is constructed with its center at the midpoint of the vector **C**, Eq. (15) may be shown to be equivalent to the statement that the point P (Fig. 1) must lie on the surface of the sphere. A cross section of this geometrical construction is shown in Fig. 2. R may be $\gtreqless C$ but if R becomes imaginary (Eq. (18)) there can occur no transitions.

To evaluate N_ρ (Eq. (12)) we have yet to perform an integration over $\mathbf{k}'$. Fig. 2 suggests that this integration be split into spherical components by the substitution

$$d\tau_{\mathbf{k}'}=dRd\sigma,$$

where $d\sigma$ is a spherical surface element. Let us now perform the integration with respect to R. Since $F(\epsilon_\rho t)$ is a much more rapidly varying function than any other term in Eq. (12), we may consider the other terms to be constant for this integration. Thus we wish to evaluate

$$\int F(\epsilon t)dR=\int\frac{F(\epsilon t)d(\epsilon t)}{d(\epsilon t)/dR}.$$

From Fig. 2

$$k'^2+K'^2=2R^2+\tfrac{1}{2}C^2=2mE_{\mathbf{k}',\,\mathbf{K}'}/\hbar^2 \tag{19}$$

or, from (3),

$$2R^2+\tfrac{1}{2}C^2=(\hbar\epsilon+E_{\mathbf{k},\,\mathbf{K}})\cdot 2m/\hbar^2;$$

$$\therefore\quad d(\epsilon t)/dR=2R\cdot\hbar t/m.$$

Hence we may write

$$\int F(\epsilon t)dR=\frac{m}{2\hbar t}\cdot\frac{1}{R}\int F(\epsilon t)d(\epsilon t), \tag{20}$$

where, from (9),

$$\int F(\epsilon t)d(\epsilon t)=\int_{-\infty}^{+\infty}\frac{2(1-\cos x)}{x^2}dx=2\pi;$$

therefore, from Eq. (20),

$$\int F(\epsilon t)dR=\frac{1}{t}\cdot\frac{\pi m}{\hbar}\cdot\frac{1}{R}.$$

Thus the first integration of Eq. (12) yields

$$dN_\rho=J_p\Omega t\cdot\frac{2m^2e^4}{\hbar^4}\rho_l(\mathbf{k})\frac{1}{R}\frac{1}{K}\times\left(\frac{1}{S_\rho{}^4}\Big|\sum_{\mathbf{m}}a_{\rho+\mathbf{m}}(\mathbf{k})a_{\mathbf{m}}{}^*(k')\Big|^2\right)d\sigma. \tag{21}$$

Consider the variable part of Eq. (21)—i.e., the expression within the brackets. The summation of the Fourier components of the unperturbed lattice eigenfunctions is a term which would not be expected to exhibit any very pronounced dependence on $\mathbf{k}'$. $1/S^4$, on the other hand, turns out to have values differing importantly from zero over only a small fraction of the surface of our sphere. This may be seen from the following considerations.

In Fig. 3 the vector **C** is shown resolved into its components $\mathbf{k}+2\pi\boldsymbol{\varrho}/a$ and **K**. If we define

$$\begin{aligned}\mathbf{A}&=\tfrac{1}{2}\mathbf{C}-(\mathbf{k}+2\pi\boldsymbol{\varrho}/a)\\&=\tfrac{1}{2}(\mathbf{K}+\mathbf{k}+2\pi\boldsymbol{\varrho}/a)-(\mathbf{k}+2\pi\boldsymbol{\varrho}/a),\end{aligned}$$

then

$$A^2=\tfrac{1}{4}[K^2-2\mathbf{K}\cdot(\mathbf{k}+2\pi\boldsymbol{\varrho}/a)+(\mathbf{k}+2\pi\boldsymbol{\varrho}/a)^2]. \tag{22}$$

Now, from Eqs. (16), (17) and (18),

$$R^2=\tfrac{1}{4}[K^2-2\mathbf{K}\cdot(\mathbf{k}+2\pi\boldsymbol{\varrho}/a)+k^2-(2\pi\boldsymbol{\varrho}/a)^2-2\mathbf{k}\cdot 2\pi\boldsymbol{\varrho}/a]. \tag{23}$$

From Eqs. (22) and (23)

$$A^2=R^2+\tfrac{1}{2}\cdot 2\pi\boldsymbol{\varrho}/a\cdot[2\pi\boldsymbol{\varrho}/a+2\mathbf{k}]. \tag{24}$$

Now S is the length of the vector which joins the point Q (Fig. 3) to a point P on the sphere. Evidently the minimum possible value of S is

$$S_{\min}=A-R. \tag{25}$$

If the primary electrons are of high energy (this assumption will be examined shortly) so that $2\pi\varrho/a\ll K$ and $k\ll K$, then $R\sim\tfrac{1}{2}K$ and Eq. (24)

may be expanded to give

$$A \sim R + \left(\frac{1}{4} \frac{2\pi\boldsymbol{\rho}/a \cdot [2\pi\boldsymbol{\rho}/a + 2\mathbf{k}]}{R^2}\right) R \qquad (26)$$

or

$$S_{\min} \sim \left(\frac{1}{4} \frac{2\pi\boldsymbol{\rho}/a \cdot [2\pi\boldsymbol{\rho}/a + 2\mathbf{k}]}{R^2}\right) R. \qquad (27)$$

Since $2\pi\rho/a \ll R$,

$$S_{\min} \ll R.$$

Inasmuch as $1/S^4$ appears in Eq. (21), it is clear that the right side of the equation will have large values over only a small fraction of the surface of our sphere—i.e., when PP' (See Fig. 3) $\lesssim (2\pi\boldsymbol{\rho}/a) \cdot [2\pi\boldsymbol{\rho}/a + 2\mathbf{k}]/K$. This conclusion is of considerable physical importance. It means that, for a given $\mathbf{k}$, $\mathbf{K}$ and $\boldsymbol{\rho}$, transitions are probable only to final states for which $\mathbf{k}' \sim \mathbf{O'P'}$ (See Fig. 3), where $\mathbf{O'P'}$ differs from the vector $\mathbf{k} + 2\pi\boldsymbol{\rho}/a$ only by terms very much smaller than this vector. When, at the end of the present manipulations, we sum our results over all possible values of $\boldsymbol{\rho}$, this will mean that, when primary electrons of wave number $\mathbf{K}$ interact with lattice electrons of wave number $\mathbf{k}$, the lattice electrons are finally left in discrete groups, one group belonging to each of the possible values of $\boldsymbol{\rho}$.

An immediate consequence of the conclusion that $1/S^4$ has important values over only a small region of our sphere is that, in integrating Eq. (21), we can safely treat the Fourier terms as constants. We are left with $\int d\sigma/S^4$ to evaluate. This can easily be integrated over the surface of the sphere. The result is

$$\int \frac{d\sigma}{S^4} = \frac{4\pi R^2}{(A^2 - R^2)^2}. \qquad (28)$$

Or, from Eq. (24),

$$\int \frac{d\sigma}{S^4} = \frac{16\pi R^2}{[(2\pi\boldsymbol{\rho}/a) \cdot (2\pi\boldsymbol{\rho}/a + 2\mathbf{k})]^2}.$$

Thus the integration of Eq. (21) has given

$$\frac{1}{\Omega} \frac{dN_\rho}{dt} = \frac{16\pi m^2 e^4}{\hbar^4} \rho_l(\mathbf{k}) \frac{J_p[2R/K]_\rho}{[(2\pi\boldsymbol{\rho}/a) \cdot (2\pi\boldsymbol{\rho}/a + 2\mathbf{k})]^2}$$
$$\times \left| \sum_{\mathbf{m}} a_{\rho+\mathbf{m}}(\mathbf{k}) a_{\mathbf{m}}^*(\mathbf{k} + 2\pi\boldsymbol{\rho}/a) \right|^2, \qquad (29)$$

where N_ρ/t has been replaced by dN_ρ/dt, to indicate that our result really expresses the time rate at which lattice electrons are being knocked into new states. For large K, $2R/K = 1$, and Eq. (29) does not involve the energy of the bombarding primaries.

The complete solution of our problem is obtained by summing Eq. (29) over all possible values of $\boldsymbol{\rho}$. But now the work of Morse[7] indicates that the coefficients $a_{\mathbf{n}}$ of the Fourier expansion of the lattice eigenfunctions diminish rapidly with increasing $|n|$ and that, even for $|n| = 1$, $a_{\mathbf{n}} a_{\mathbf{n}}^* \sim 10^{-2}$, as compared with $a_{000} a^*_{000} \sim 1$. This means that

$$\left| \sum_{\mathbf{m}} a_{\rho+\mathbf{m}}(\mathbf{k}) a_{\mathbf{m}}^*(\mathbf{k} + 2\pi\boldsymbol{\rho}/a) \right|^2$$
$$\sim | a_\rho(\mathbf{k}) a_{000}^*(\mathbf{k} + 2\pi\boldsymbol{\rho}/a) + a_{000}(\mathbf{k}) a_\rho^*(\mathbf{k} + 2\pi\boldsymbol{\rho}/a) |^2$$
$$\sim | a_\rho(\mathbf{k}) + a_{-\rho}^*(\mathbf{k} + 2\pi\boldsymbol{\rho}/a) |^2 \equiv | b_\rho(\mathbf{k}) |^2. \qquad (30)$$

Evidently, further, $|b_\rho(\mathbf{k})|^2$ diminishes with increasing $|\boldsymbol{\rho}|$. In addition, the denominator in (29) increases rapidly with increasing $|\rho|$. Hence a pretty good first approximation to the solution of our problem should be afforded by a consideration of only the values

$$\boldsymbol{\rho} = 0,\ 0,\ \pm 1,$$
$$\boldsymbol{\rho} = 0,\ \pm 1,\ 0,$$
$$\boldsymbol{\rho} = \pm 1,\ 0,\ 0.$$

A great deal of the following discussion will be based upon this approximation.

In deriving Eq. (29) K has been assumed to be large, compared with $2\pi/a$ and k. Let us now examine this restriction on the range of applicability of our result.

For the usually observed secondaries, $\mathbf{k}'$ and $\mathbf{K}$ point approximately in opposite directions. Since we have seen that $\mathbf{k}' \sim \mathbf{k} + 2\pi\boldsymbol{\rho}/a$, this

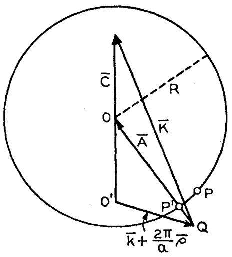

FIG. 3. Diagram showing how $S_{\min}$ is determined.

---

[7] P. M. Morse, Phys. Rev. **35**, 1311 (1930).

means that $R \lesssim \frac{1}{2}K$, as given by Eq. (23), as long as $|\mathbf{K}| > |\mathbf{k}+2\pi\boldsymbol{\varrho}/a|$. For these considerations we may set $\mathbf{k}=0$, not merely because $k<2\pi/a$, but also because $\mathbf{k}\cdot\boldsymbol{\varrho}$ is as often positive as negative and therefore has an average value of zero. Thus we may conclude that the expansion of Eq. (26) is valid as long as

$$\frac{(2\pi\boldsymbol{\varrho}/a)^2}{K^2} \ll 1.$$

If this fraction is, say, $\sim\frac{1}{4}$, the conclusion that $1/S^4$ has a large value over only a small fraction of our sphere will be a pretty good one and the consequent neglect of the variation of the Fourier components in the integration, as well as the conclusion that $\mathbf{k}'=\mathbf{k}+2\pi\boldsymbol{\varrho}/a$, will be good enough for our purposes. For silver, for example, $(\hbar^2/2m)(2\pi/a)^2\sim 25$ ev. This means that, for the calculation corresponding to $|\rho|=1$, our results should be good down to a primary energy of, say, 100 ev. For the calculations corresponding to $|\rho|>1$, the results become accurate only for higher values of primary voltage. However we have seen that the cases for which $|\rho|>1$ are of only secondary importance and for a first approximation can be neglected.

A more detailed investigation shows that, even when $|\mathbf{k}+2\pi\boldsymbol{\varrho}/a|\sim K$, and when $\mathbf{k}'$ and $\mathbf{K}$ do not point in opposite directions, the important region for $1/S^4$ is still sufficiently small that the neglect of the variation of the Fourier components in the integration, as well as the conclusion that $\mathbf{k}'\sim\mathbf{k}+2\pi\boldsymbol{\varrho}/a$, are fair approximations (as far as the use to which they will be put is concerned). For this range the factor $[2R/K]_\rho$ in Eq. (29) expresses the dependence on K of the results of the bombardment. Eq. (23) provides an explicit expression of this dependence. Since we will be concerned only with bombarding energies considerably greater than the Fermi energy of the electrons, we may neglect k^2/K^2 compared to one, in which case Eq. (23) may be written

$$F_\rho(\mathbf{k},\mathbf{K}) \equiv \left[\frac{2R}{K}\right]_\rho = \left[1-\frac{(\mathbf{k}+2\pi\boldsymbol{\varrho}/a)^2}{K^2}-\frac{2\mathbf{K}\cdot(\mathbf{k}+2\pi\boldsymbol{\varrho}/a)}{K^2}\right]^{\frac{1}{2}}. \quad (31)$$

In terms of Eqs. (30) and (31), Eq. (29) now becomes

$$\frac{1}{\Omega}\frac{dN_\rho}{dt} = \frac{16\pi m^2 e^4}{\hbar^4}\rho_l(\mathbf{k})J_p \times \frac{|b_\rho(\mathbf{k})|^2}{[(2\pi\boldsymbol{\varrho}/a)\cdot(2\pi\boldsymbol{\varrho}/a+2\mathbf{k})]^2}F_\rho(\mathbf{k},\mathbf{K}). \quad (32)$$

This equation should be reasonably valid down to the lowest bombarding energies we shall need to consider. The dependence of dN_ρ/dt on K is small and not at all of the right form to account for the observed shape of secondary yield *vs.* bombarding voltage curves.

At this point the effect of the exclusion principle may be disposed of. Besides requiring the use of Fermi statistics in summing the results over all the lattice electrons, the exclusion principle, as Fröhlich pointed out, forbids any final state for which either k' or K' is less than $k_{\max}$, the value of k corresponding to the top of the Fermi distribution in the metal. This is equivalent to the requirement that $(\hbar^2/2m)k'^2$ and $(\hbar^2/2m)K'^2$ must each exceed $E_{\max}\equiv(\hbar^2/2m)(k_{\max})^2$. Since, for the final states of interest, $\mathbf{k}'=\mathbf{k}+2\pi\boldsymbol{\varrho}/a$, where $|\rho|=1$, a lattice electron, on the average, absorbs energy of amount (very nearly).

$$E_0 \equiv (\hbar^2/2m)(2\pi/a)^2$$

from the primary electron which collides with it. Thus the exclusion principle requires that the production of secondaries fall off rapidly when

$$E_p \lesssim E_0 + E_{\max}.$$

For silver, $E_0\sim 25$ ev and $E_{\max}\sim 5$ ev. We should therefore expect the secondary emission to drop rapidly to zero when the bombarding energy E_p (measured *inside* the target) drops below 25 or 30 ev.

Free electron approximation

Before proceeding with the development it is necessary to examine the free electron approximation in the light of the foregoing results. If we start with Eq. (21) and carry out the appropriate computation, assuming $|\mathbf{k}|\ll|\mathbf{K}|$, we

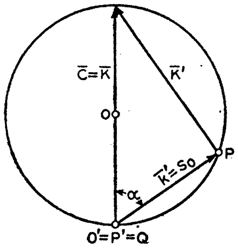

FIG. 4. Special case of momentum principle for which $\rho=0$.

obtain

$$\frac{1}{\rho_l J_p}\frac{1}{\Omega t}(dN_0)_{\text{tot}}$$

$$=\frac{e^4}{m^2V^4}(\sec^4\alpha+\csc^4\alpha)4\cos\alpha d\omega. \quad (33)$$

This is the familiar Rutherford scattering formula, which is precisely the result which one must get when, as here, the Born approximation is used and the exclusion principle is neglected.[8]

While Eq. (33) can tell us nothing about the usual type of backward secondary emission, it is of importance in any attempt to predict the production of forward secondaries, which might be observed by the use of thin foils as targets. Eq. (33) divides the scattered electrons into two almost distinct groups—(a) electrons which, after collision, differ only slightly in energy and direction from the primary beam and (b) electrons which are knocked into states of much lower energy and which move away from the primary beam at angles >45°. If we consider the first group of electrons to be left exactly, rather than approximately, in the primary beam after the collision, and calculate the rate at which electrons are produced in the second group with energies and directions which make it possible for them to escape from the back side of the target, we should arrive at a rough estimate of the importance of the free electron approximation in the production of forward secondaries. For normal incidence such a calculation merely involves the integration[9] of Eq. (33) between the limits $\alpha=\pi/4$ and $\alpha=\alpha_{\max}$, where $\alpha_{\max}$ is the angle for which the component of the energy of the electron normal to the target surface (parallel to **K**) is just equal to the energy W_a necessary for escape from the surface. From Fig. 4 it is clear that the energy of an electron scattered into the angle α is $E_p\cos^2\alpha$, where E_p is the primary energy. Hence

$$(E_p\cos^2\alpha_{\max})\cos^2\alpha_{\max}=W_a$$

or

$$\cos^2\alpha_{\max}=(W_a/E_p)^{\frac{1}{2}}.$$

For the rate of production of electrons which can escape from the back of the target if not further scattered, Eq. (33) gives (setting $m^2V^4=4E_p^2$)

$$\frac{1}{\rho_l J_p}\frac{1}{\Omega t}\int(dN_0)_{\text{tot}}$$

$$=\frac{e^4}{E_p^2}\int_{\alpha=\pi/4}^{\alpha_{\max}}(\sec^4\alpha+\csc^4\alpha)\cos\alpha d\omega$$

$$\sim\frac{\pi e^4}{E_p^2}\left[\left(\frac{E_p}{W_a}\right)^{\frac{1}{2}}-1\right]. \quad (34)$$

To obtain (34) the approximation $W_a \ll E_p$ has been employed.

From Eq. (32), the corresponding rate of production of forward electrons due to the "bound" term for which $|\rho|=1$ and $\boldsymbol{\rho}$ and **K** coincide in direction (assuming **K** to be directed along one of the axes of our simple cubic lattice) is

$$\frac{1}{\rho_l J_p}\frac{1}{\Omega t}(N_1)\sim\frac{16\pi m^2e^4}{\hbar^4}\frac{|b_1(\mathbf{k})|^2}{(2\pi/a)^4}. \quad (35)$$

This equation also assumes E_p to be large. $|b_1(\mathbf{k})|^2$ is to be thought of as an average $|b_1|^2$ over all the lattice electrons. If we replace $\hbar^4/m^2$ by $4E_p^2/K^4$, Eq. (35) becomes

$$\frac{1}{\rho_l J_p}\frac{1}{\Omega t}(N_1)\sim\frac{4\pi e^4}{E_p^2}\frac{|b_1(\mathbf{k})|^2}{(2\pi/aK)^4}.$$

Or, since

$$(2\pi/aK)^4=(E_0/E_p)^2,$$

$$\frac{1}{\rho_l J_p}\frac{1}{\Omega t}(N_1)\sim\frac{4\pi e^4}{E_p^2}\frac{|b_1(\mathbf{k})|^2}{(E_0/E_p)^2}. \quad (36)$$

---

[8] N. E. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford, 1933), p. 76.

[9] The neglect of the exclusion principle does not produce a serious error in such an integration. See, for example, N. E. Mott and H. S. W. Massey, reference 8, pp. 73–74.

Dividing Eq. (36) by (34) gives

$$\frac{N_1}{N_0}=\frac{4|b_1(\mathbf{k})|^2(E_p/E_0)^2}{[(E_p/W_a)^{\frac{1}{2}}-1]}.$$

For silver bombarded by 400-volt primaries, the ratio becomes

$$N_1/N_0 \sim 500|b_1(\mathbf{k})|^2. \tag{37}$$

From the work of Morse[7] we would guess that $|b_1(\mathbf{k})|^2 \sim 10^{-2}$ and from some of the results reached later in this paper we will find reason to believe that $|b_1(\mathbf{k})|^2$ may be somewhat larger than this value. Eq. (37), from the nature of its calculation, can by no means be considered a precise result, but it is probably accurate enough to justify the conclusion that, even in the production of forward secondary electrons, in spite of the smallness of the higher Fourier components, the free electron term may not be of much importance.

This conclusion leads one to suspect that perhaps even the rate of loss of energy of the primaries might be determined principally by the terms in our expansion for which $\rho \neq 0$. If a calculation is made, similar to the above, on the rate at which the primary beam loses energy by "free electron" scattering, one finds indeed that the mean free path of electrons of a few hundred volts energy so predicted is much higher than that which is observed. In such a calculation, however, the inaccuracies are so great that the result cannot be taken too seriously. Fortunately there exists much more convincing evidence on this point.

Consider again, for example, the case of silver. When it is bombarded by 400-volt electrons the backward yield of secondaries is 1.5[10]—i.e., for every primary electron which strikes the surface, 1.5 secondaries are observed. We have seen that each secondary, on the average, absorbs about 25 ev of energy from the primary electron which creates it. Since the mean Fermi energy is only ~3 ev, the secondaries will be created with a mean energy of ~25–30 ev. Those which can escape have their directions confined within a rather small solid angle around the normal to the surface. For silver, this solid angle $\sim 4\pi/5$. Thus, for every secondary electron observed, four more (assuming random orientation of the crystallites), are produced which cannot escape, even if no absorption occurs. This means that, within a distance from the surface of the target approximately equal to the reciprocal of the absorption coefficient of the 25-volt secondaries, $5\times 1.5 \sim 8$ secondaries are created by every primary electron. The energy required is $8\times 25=200$ ev. *This means that a 400-volt primary would have an absorption coefficient about one-half as large as that of a 25-volt secondary*, due to this cause alone. But a calculation of the relative absorption coefficients from the "free electron" formula, Eq. (33), would yield a ratio of ~1 : 100, instead of 1 : 2. Although Eq. (33) is not accurate for a calculation of this type, it seems unlikely that a correct calculation based on the free electron approximation could predict a rate of loss of energy of the primaries of this order. Hence it seems safe to conclude that, when electrons of a few hundred volts energy travel through a metal, they lose energy principally by the production of secondaries[11] (corresponding to $\rho \neq 0$), until their energy becomes too small to produce any further secondaries (for Ag, ~25 ev). For the remainder of their path, probably the rate of loss of energy is determined by "free electron" scattering.

Limitations on the applicability of the results

In attempting to apply Eq. (32) to an interpretation of experimental data, one would like to commence with some sort of averaging process over all the lattice electrons which would make it unnecessary to deal further with a function of $\mathbf{k}$. But, for a chosen direction of $\boldsymbol{\rho}$, there may exist a few electrons having momenta of such directions and magnitudes that $(2\pi\boldsymbol{\rho}/a)\cdot(2\pi\boldsymbol{\rho}/a+2\mathbf{k})=0$. (For such electrons evidently $\mathbf{k}$ lies on the surface of a Brillouin zone.) Eq. (32) would appear to assign to these electrons an infinite probability of being knocked into the new state $\mathbf{k}' \sim \mathbf{k}+2\pi\boldsymbol{\rho}/a$. It is easy to establish, however, that such a selectivity effect does not occur. We have employed an approximation which is not valid in this case. The integration of Eq. (4) breaks down when S becomes too small and, for the electrons in question, $S_{\min}\rightarrow 0$. A detailed consideration of

---

[10] H. Bruining and J. H. de Boer, Physica 5, 17 (1938).

[11] From this point on we will speak of the bundles of electrons corresponding to $\boldsymbol{\rho}\neq 0$ as secondary electrons. Those which escape from the target will be referred to as "observed" or "emitted" secondary electrons.

this matter removes from the picture any likelihood that the secondaries are produced mainly from the lattice electrons whose $\mathbf{k}$ vector lies on the surface of a Brillouin zone. In fact, it will be a good enough approximation for most of the following development if we treat the problem as if $\mathbf{k}\cdot\boldsymbol{\rho}=0$. Then Eq. (32) becomes (for $\rho=1$)

$$\frac{1}{\Omega}\frac{dN_\rho}{dt}=\frac{16\pi m^2e^4}{\hbar^4}\rho_l J_p\frac{|b_\rho|^2}{(2\pi/a)^4}F_\rho(\mathbf{K}), \tag{38}$$

where now it will be accurate enough to write

$$F_\rho(\mathbf{K})\equiv\left[1-\frac{(2\pi/a)^2+2mE_F/\hbar^2}{K^2}-\frac{2\mathbf{K}\cdot(2\pi\boldsymbol{\rho}/a)}{K^2}\right]^{\frac{1}{2}}. \tag{39}$$

Eq. (38) is to be interpreted as follows. A current of primary electrons of number J_p per cm^2 per sec. and of momentum $\hbar\mathbf{K}$, travels through a simple cubic lattice, of principal axes (1, 0, 0), (0, 1, 0), and (0, 0, 1). Corresponding to each of the six directions $\boldsymbol{\rho}=(1, 00)$, $(-1, 0, 0)$, etc. a group of secondary electrons is produced, at a rate given by Eq. (38). On the average, the energy of a secondary electron is $E_F+(\hbar^2/2m)(2\pi/a)^2$, where E_F is the mean Fermi energy of the lattice electrons and $(\hbar^2/2m)(2\pi/a)^2$ is the average energy lost by a primary electron in producing one secondary. For a given $\boldsymbol{\rho}$, the secondaries have their directions bunched around the direction of $\boldsymbol{\rho}$. If $2\pi/a\gg k_{\max}$, the spread in energies and directions will be small. In the case of silver, $k_{\max}\sim\frac{1}{2}\cdot 2\pi/a$, so we must expect each group to contain secondaries of energies up to

$$\frac{\hbar^2}{2m}\left(\frac{1}{2}\cdot\frac{2\pi}{a}+\frac{2\pi}{a}\right)^2\sim 2\times\frac{\hbar^2}{2m}\left(\frac{2\pi}{a}\right)^2.$$

Thus, each group of secondaries contains a few electrons of energies up to 40 or 50 ev.

In Eq. (38), ρ_l now represents the total electron density, while $|b_\rho|^2$ is to be thought of as the value of $|b_\rho(\mathbf{k})|^2$ averaged over all the lattice electrons.

One other effect of our approximations must be mentioned. Eq. (4) was found to be inapplicable when $S_{\min}\rightarrow 0$. But, even though $\mathbf{k}\cdot\boldsymbol{\rho}=0$, $S_{\min}$ becomes very small when K becomes very large (Eq. 27). Consequently, for large K our calculations will not hold. It is possible to predict that the secondary yield will fall off for high primary energies, from qualitative considerations. Semi-quantitative calculations of some length can be carried out which predict that, for silver, this falling off should commence for $E_p\sim 1000$ ev, but such calculations cannot be regarded as accurate.

II. Application of the Results

For this development we shall employ the following results of the foregoing treatment:

(1) Eqs. (38) and (39) with the interpretation written below them.

(2) The conclusion that, when electrons of energies up to a few hundred volts travel through a metal, they lose energy principally by the production of secondaries according to Eq. (38), until their energy becomes $\sim(\hbar^2/2m)(2\pi/a)^2$ (~ 25 ev, for silver).

In addition we shall assume that the target is composed of many crystallites, or grains, of random orientation, so that the vector $\boldsymbol{\rho}=(1,0,0)$, for example, has equal probabilities of pointing in all directions relative to the target surface. The fraction of all the crystallites which have one of their six directions for $|\rho|=1$ within the solid angle $d\omega$, making an angle θ with the normal to the target surface, is $6d\omega/4\pi$. Thus, on the average, a volume element $d\Omega$, in time dt, emits a number of secondaries dN of directions included within the solid angle $d\omega$ at an angle θ with the normal to the target surface where, from Eq. (38)

$$dN=\frac{16\pi m^2e^4}{\hbar^4}J_p\rho_l\frac{|b_1|^2}{(2\pi/a)^4}F_1(K,\theta)6\frac{d\omega}{4\pi}d\Omega dt \tag{40}$$

$|b_1|^2$, of course, represents $|b_{1,0,0}|^2=|b_{0,1,0}|^2$, etc. For normal incidence, from Eq. (39)

$$F_1(K,\theta)=\left[1-\frac{(2\pi/a)^2+2mE_F/\hbar^2}{K^2}+\frac{2}{K}\frac{2\pi}{a}\cos\theta\right]^{\frac{1}{2}}. \tag{41}$$

We are now ready to derive an expression for the observed secondary yield as a function of the bombarding voltage. We are here concerned with the fraction of the dN of Eq. (40) which actually escape from the bombarded surface. If $d\Omega$ lies directly in the surface of the target, then the secondaries which can escape are those emitted so that their directions make angles of less than $\theta_{\max}$ with the normal to the surface, where

$$(E_0+E_F)\cos^2\theta_{\max}=W_a.$$

W_a is the normal component of energy with which an electron must approach the surface in order to escape ($W_a=$max. Fermi Energy $E_{\max}$ plus work function χ), E_F is the mean Fermi energy, while E_0 is the average energy given by the primary electron to a secondary:

$$E_0=(\hbar^2/2m)(2\pi/a)^2.$$

The fraction of the secondaries which can escape is, from Eq. (40)

$$f=\frac{\displaystyle\int_{\theta=0}^{\theta_{\max}}F_1(K,\theta)\frac{d\omega}{4\pi}}{\displaystyle\int_0^{\pi}F_1(K,\theta)\frac{d\omega}{4\pi}}. \tag{42}$$

With the help of Eq. (41), this can be evaluated. The result may be expanded as

$$f=\frac{1}{2}\left\{1-\left(\frac{W_a}{E_0+E_F}\right)^{\frac{1}{2}}\right\}+\frac{1}{4}\frac{2\pi}{aK}\left\{1-\frac{W_a}{E_0+E_F}\right\}+0\left|\left(\frac{2\pi}{aK}\right)^2\right|. \tag{43}$$

The two terms given will be adequate for our purposes. In the same way it can be shown that

$$\int_0^{\pi}F_1(K,\theta)\frac{d\omega}{4\pi}=1+0\left|\left(\frac{2\pi}{aK}\right)^2\right|. \tag{44}$$

In the absence of knowledge of the exact form of the scattering or absorption law for the secondary electrons, it should not be far wrong to assume an exponential relation. If we do so we may write, for the fraction of the secondaries emitted in the volume element $d\Omega$, located a distance x beneath the target surface, which escape from the target,

$$g(x)=f(x)e^{-\gamma_s x}, \tag{45}$$

where $f(x)$ is obtained from Eq. (43) by assigning to K the value left to the primary particles after they have penetrated to a depth x.[12]

From Eqs. (40), (42), (44) and (45) we obtain an expression for the observed secondary emission coefficient δ (number of secondaries per primary):

$$\delta=\frac{96\pi m^2e^4}{\hbar^4}\rho_l\frac{|b_1|^2}{(2\pi/a)^4}\int_0^{l(E_p)}f(x)e^{-\gamma_s x}dx. \tag{46}$$

$l(E_p)$ is the distance the primary electrons, which enter the target with energy E_p (measured just *under* the surface), travel before they become too slow to produce secondaries—i.e., when their energy $\rightarrow E_0$.

When the bombarding voltage is high,

$$f(x)\rightarrow\tfrac{1}{2}\left\{1-\left(\frac{W_a}{E_0+E_F}\right)^{\frac{1}{2}}\right\}$$

and we get

$$\delta_\infty=\frac{96\pi m^2e^4}{\hbar^4}\rho_l\frac{|b_1|^2}{(2\pi/a)^4}\frac{\frac{1}{2}\{1-(W_a/(E_0+E_F)^{\frac{1}{2}}\}}{\gamma_s}. \tag{47}$$

For silver we may take the approximate values: $W_a=10$ ev; $a=3\times10^{-8}$ cm; $E_0=25$ ev. From Becker's measurements[13] we may conclude that $\gamma_s\sim2\times10^6$ cm^{-1}. For ρ_l we must take $1/a^3$, corresponding to one valence electron per unit cell. The result is

$$\delta_\infty\sim20|b_1|^2.$$

Since, for silver, $\delta_\infty\sim1.5$, we require that $|b_1|^2\sim0.07$. From Eq. (30) it is evident that $|b_1|^2$ may be as high as $4|a_1|^2$ where, from the work of Morse, we expect that $|a_1|^2\sim10^{-2}$. The value required here appears therefore to be a reasonable one.

Let us return now to Eqs. (46) and (47).

---

[12] We are not assuming here that the secondary electrons reach the surface with their initial energies and directions, or that the absorption coefficient is the same for all secondaries. Our assumption is simply that, on the average, the probability that a secondary electron escapes depends on the depth at which it originated through an exponential relation, modified by the behavior of $f(x)$.

[13] A. Becker, Ann. d. Physik 5, 2, 249 (1929).

Dividing them, we obtain

$$\frac{\delta}{\delta_\infty}=\gamma_s\frac{\int_0^{l(E_p)} f(x)e^{-\gamma_s x}dx}{\frac{1}{2}\{1-(W_a/(E_0+E_F)^{\frac{1}{2}}\}}.$$

From Eq. (43) this may be written

$$\frac{\delta}{\delta_\infty}=\{1-\exp\left[-1\gamma_s l(E_p)\right]\}+\frac{1}{2}\left\{1+\left(\frac{W_a}{E_0+E_F}\right)^{\frac{1}{2}}\right\}$$

$$\times\int_0^{l(E_p)}\frac{2\pi}{aK(x)}\exp\left(-\gamma_s x\right)\gamma_s dx. \quad (48)$$

To determine $l(E_p)$ and $E(x)$ we proceed as follows. The number of secondaries produced by a primary electron in traveling the distance dx in the target may be gotten from Eqs. (40) and (44). It is

$$dn=\frac{96\pi m^2e^4}{\hbar^4}\rho_l\frac{|b_1|^2}{(2\pi/a)^4}dx.$$

The energy thus lost by the primary is

$$-dE=E_0 dn$$

or

$$-dE=E_0\cdot\frac{96\pi m^2e^4}{\hbar^4}\rho_l\frac{|b_1|^2}{(2\pi/a)^4}dx. \quad (49)$$

When the primary electron has traveled a distance

$$l(E_p)=\frac{E_p-E_0}{-dE/dx}, \quad (50)$$

its energy is only E_0 and it produces no more secondaries. From (49), (50) and (47),

$$l(E_p)=\frac{\frac{1}{2}\{1-(W_a/(E_0+E_F))^{\frac{1}{2}}\}}{\gamma_s\delta_\infty}\left\{\frac{E_p}{E_0}-1\right\}. \quad (51)$$

This is the required expression for l. For $E(x)$, Eqs. (49) and (47) give

$$E(x)=E_p-x\cdot E_0\frac{\gamma_s\delta_\infty}{\frac{1}{2}\{1-(W_a/(E_0+E_F))^{\frac{1}{2}}\}}$$

or

$$\frac{E(x)}{E_0}=\frac{E_p}{E_0}-\frac{\delta_\infty(\gamma_s x)}{\frac{1}{2}\{1-(W_a/(E_0+E_F))^{\frac{1}{2}}\}}. \quad (52)$$

Equations (48), (51) and (52) may now be combined to give

$$\frac{\delta}{\delta_\infty}=\left\{1-\exp\left[-\frac{\frac{1}{2}\{1-(W_a/(E_0+E_F))^{\frac{1}{2}}\}}{\delta_\infty}\left(\frac{E_p}{E_0}-1\right)\right]\right\}$$

$$+\frac{1}{2}\left\{1+\left(\frac{W_a}{E_0+E_F}\right)^{\frac{1}{2}}\right\}\int_0^{\frac{\frac{1}{2}\{1-(W_a/(E_0+E_F))^{\frac{1}{2}}\}}{\delta_\infty}\left(\frac{E_p}{E_0}-1\right)}\frac{e^{-v}dv}{\left[\frac{E_p}{E_0}-\frac{\delta_\infty v}{\frac{1}{2}\{1-(W_a/(E_0+E_F))^{\frac{1}{2}}\}}\right]^{\frac{1}{2}}}, \quad (53)$$

where $aK(x)/2\pi$ has been written as $[E(x)/E_0]^{\frac{1}{2}}$. From this equation, if we know δ_∞, we can plot the δ *vs.* E_p curve to show how the observed secondary emission coefficient depends on the bombarding voltage.

Now Eq. (53) has been derived on the assumption that the target possesses a simple cubic lattice structure. However, most of the materials of interest possess either a face-centered or a body-centered cubic structure. When the problem is considered in terms of the proper set of (nonorthogonal) coordinates which must be employed it develops that, for both the face- and body-centered cubic structures, the foregoing result should apply if "a" is assigned a value approximately ten percent less than the cube root of the atomic volume.[14] For the calculations to be made let us therefore define

$$a_0\equiv 0.9a,$$

where, in Eq. (53)

$$E_0=(\hbar^2/2m)(2\pi/a_0)^2$$

but a^3 is the volume per atom of the target material.

δ *vs.* E_p curves

1\. *Silver.*—Let us employ somewhat more accurate data than used heretofore. From

---

[14] This treatment applies also to the close-packed hexagonal lattice.

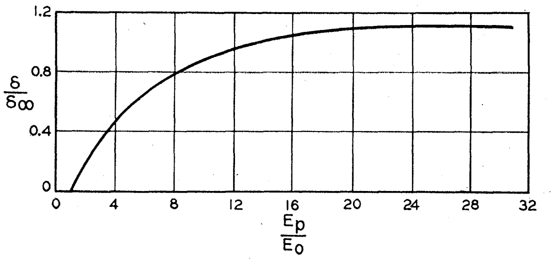

FIG. 5. First approximation to the δ/δ_∞ *vs.* E_p/E_0 curve for silver.

Mott and Jones[15] we obtain $a=2.56\times10^{-8}$ cm $\therefore$ $a_0=2.30\times10^{-8}$ cm and $E_0=28.2$ ev. For W_a we add $\chi=4.7$ ev.[16] and $E_{\max}=5.5$ ev.[17] $\therefore$ $E_F=\frac{3}{5}E_{\max}{}^{18}=3.3$ ev.

In addition to these constants we require δ_∞. This must be obtained from experiment. However δ_∞ cannot be read directly from the experimental δ *vs.* E_p curve because, as has been shown earlier, we cannot expect our equations to hold when E_p becomes very large. Fortunately, however, we can evade this difficulty as follows. First assume a reasonable value of δ_∞ (say 1.5, for Ag) and plot the resulting δ *vs.* E_p curve from Eq. (53). This curve will rise to a maximum $\delta=\delta_{\max}$ which is somewhat greater than δ_∞. Compare this value of $\delta_{\max}$ with the experimentally observed value. Then multiply δ_∞ by the ratio $(\delta_{\max})_{\text{exp}}/(\delta_{\max})_{\text{theoret}}$ and plot the corresponding curve, etc. The functions are such that adequate agreement of $(\delta_{\max})_{\text{exp}}$ and $(\delta_{\max})_{\text{theoret}}$ can generally be secured on the first or second attempt. By this method of successive approximations the theoretically derived curve is adjusted from experimental data only through the one parameter $\delta_{\max}$. There is no such adjustment of either the shape of the curve or the abscissa scale.

If, as suggested, we first try $\delta_\infty=1.5$, Eq. (53) becomes

$$\frac{\delta}{\delta_\infty}=1-\exp\left[-0.145(E_p/28\text{ev}-1)\right]+0.78\int_0^{0.145(E_p/28\text{ev}-1)}\frac{e^{-v}dv}{\left[E_p/28\text{ev}-6.9v\right]^{\frac{1}{2}}}.$$

The last term can be treated graphically. The result is plotted as Fig. 5. From this curve $\delta_{\max}=1.13\delta_\infty=1.70$. Experimentally,[10] $\delta_{\max}=1.57$. Let us therefore take $\delta_\infty=(1.57/1.70)\times1.5=1.39$. The resulting curve requires only a very small further correction of δ_∞. The final result is plotted as the solid curve of Fig. 6. The experimental points are taken from the measurements of Bruining and de Boer[10] on evaporated silver.[19] The agreement is probably better than the accuracy of the theoretical derivation. It is important to observe that the *only* quantity taken from experimental secondary emission data for plotting the theoretical curve is $\delta_{\max}$. Presumably even $\delta_{\max}$ could be evaluated theoretically if accurate data were available on the lattice fields in the target.

In Figs. (7) to (13), inclusive, are shown similar comparisons of theory with the other data given by Bruining and de Boer for evaporated targets of pure metals. The constants used in these calculations are collected in Table I.

Except for the cases of caesium and barium (to be discussed below), the agreement between experiment and theory is as good as could be expected. It is probably significant that the agreement is best for copper and silver, which exhibit a practically constant δ over a wide range of values of E_p. For the other metals treated (except Cs and Ba) the theoretical curve always rises appreciably below the experimental data. This is probably partly due to the fact that the

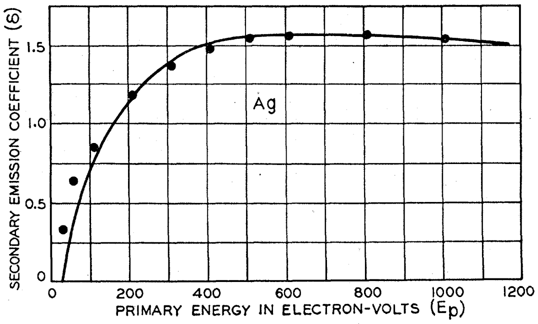

FIG. 6. Secondary yield *vs.* primary energy curve for silver. Experimental points taken from Bruining and de Boer.

---

[15] Reference 3, p. 318.

[16] A. L. Reimann, *Thermionic Emission* (John Wiley and Sons, 1934), p. 99.

[17] Reference 3, p. 54.

[18] Reference 3, p. 55.

[19] In this, as in all succeeding plots, the abscissa values of the experimental points have been increased by the amount W_a, since in these plots E_p represents the primary energy just *under* the surface rather than just before impact, as measured experimentally.

calculations do not contain means of including the degradation of δ which has been shown to set in at large values of E_p. In addition, the experimental data should be corrected for the elastic reflection of the primaries which becomes important at low E_p for weakly emitting targets. Such reflection modifies the yield curve so that δ does not approach zero as E_p diminishes. This effect is exhibited particularly clearly by the experimental data for Be, Cs and Ba. The inclusion of these effects in the calculations would tend to close the gap between theory and experiment.

The discrepancy between theory and experiment is too large in the cases of caesium and barium to be accounted for by elastic reflection or by the expected degradation of δ for large E_p. It seems possible that the theory breaks down in these cases through invalidation of the assumption that the primary electrons lose energy principally by the production of secondaries. The loss of energy by Rutherford scattering is probably not entirely negligible in any case; examination of theory shows that this factor should become increasingly important as the atomic volume increases. The very large atomic volumes of caesium and barium, together with their low secondary yields, may account for the discrepancy between theory and experiment.

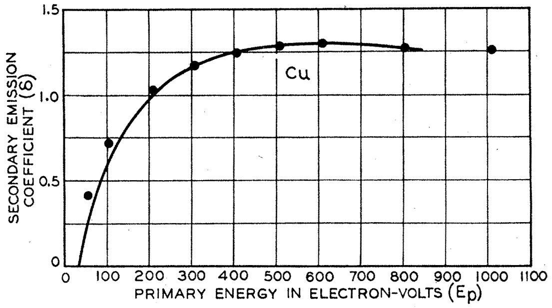

FIG. 7. Secondary yield *vs*. primary energy curve for copper. Experimental points taken from Bruining and de Boer.

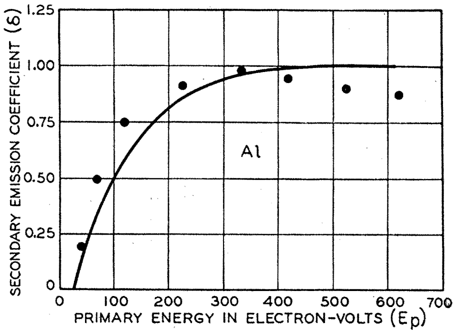

FIG. 8. Secondary yield *vs*. primary energy curve for aluminum. Experimental points taken from Bruining and de Boer.

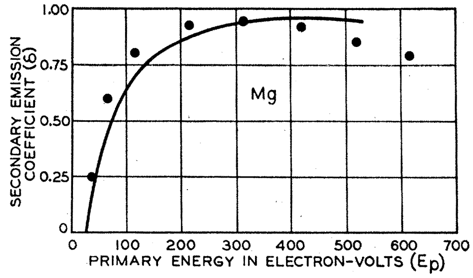

FIG. 9. Secondary yield *vs*. primary energy curve for magnesium. Experimental points taken from Bruining and de Boer.

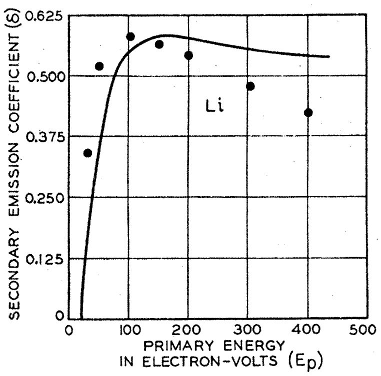

FIG. 10. Secondary yield *vs*. primary energy curve for lithium. Experimental points taken from Bruining and de Boer.

The theory set forth in this paper has been derived only for the case of targets in which the electrons are nearly free. For many pure metals this should be a good assumption, but caution must be observed in attempting to apply this theory to complex or nonmetallic surfaces. There may be many such surfaces in which the electrons behave sufficiently like free electrons to justify this extension, but in the absence of definite information such a treatment must be viewed with suspicion. Probably it is safe to conclude, however, that a complex caesium or barium surface, for example, can exhibit a very high δ for $E_p \lesssim 400$ ev only because the lattice spacing is large and E_0 is correspondingly small. Naturally, if the energy absorbed per secondary is small

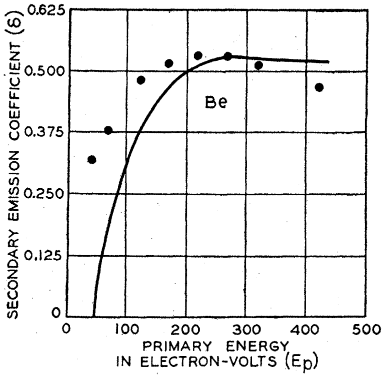

FIG. 11. Secondary yield *vs.* primary energy curve for beryllium. No correction made for elastic reflections at low energies. Experimental points taken from Bruining and de Boer.

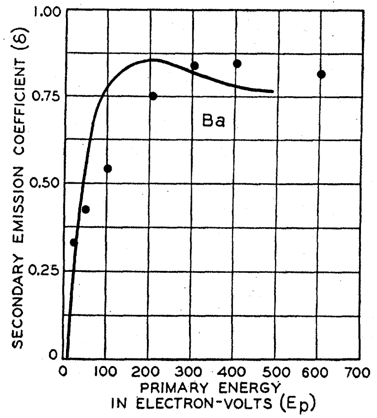

FIG. 12. Secondary yield *vs.* primary energy curve for barium. No correction made for elastic reflections at low energies. Experimental points taken from Bruining and de Boer.

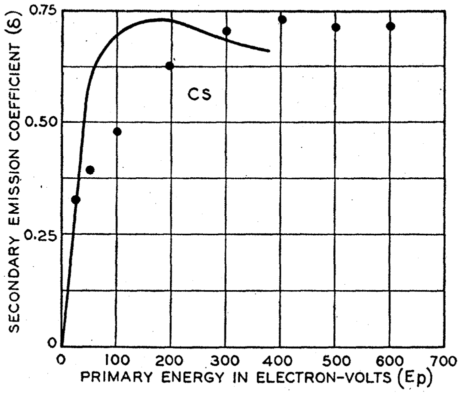

FIG. 13. Secondary yield *vs.* primary energy curve for caesium. No correction made for elastic reflections at low energies. Experimental points taken from Bruining and de Boer.

enough, δ may be very large for comparatively low values of E_p. It is probably not mere coincidence that the theory here outlined predicts δ *vs.* E_p curves for Cs_2O and BaO surfaces which are in more than qualitative agreement with experiment, when lattice constants appropriate to the targets are employed and (in the absence of any exact information) values of $E_{\max}$ and E_F appropriate to the pure metal are used. In Fig. (14) the case of BaO is illustrated. The data employed were

$$a = 5.53 \times 10^{-8}\ \text{cm}^{24}\ \text{(cubic structure)};$$
$$\therefore\ a_0 = a \text{ and } E_0 = 5.0\ \text{ev};$$
$$\chi = 1\ \text{ev};^{25}$$
$$E_{\max} = 3.6\ \text{ev};^{22}$$
$$\therefore\ E_F = 2.2\ \text{ev}.$$

Other properties of secondary emission

The approximations which have been used in deriving the foregoing curves are of such a nature as to lead to pretty good results when calculations of the total yield are made, but we would not

TABLE I.

METAL	a^{15}	E_0	χ	$E_{\max}$	$E_F = \frac{3}{5}E_{\max}$
Aluminum	2.54×10^{-8} cm	28.4 ev	3 ev[20]	16 ev[21]	9.6 ev
Barium	3.98 "	11.6 "	2.1 "[16]	3.6 "[22]	2.2 "
Beryllium	2.00 "	45.9 "	3 "	13.5 "[21]	8.1 "
Caesium	4.89 "	7.6 "	1.9 "[16]	1.5 "[17]	0.9 "
Copper	2.27 "	35.8 "	4.4 "[23]	7.1 "[17]	4.3 "
Lithium	2.77 "	23.8 "	2.3 "[16]	4.2 "[21]	2.5 "
Magnesium	2.84 "	22.8 "	2.4 "[16]	9.0 "[21]	5.4 "
Silver	2.56 "	28.2 "	4.7 "[16]	5.5 "[17]	3.3 "

---

[20] P. S. Epstein, *Textbook of Thermodynamics* (Wiley, 1937), p. 280.

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

[22] Calculated on the assumption of two free electrons per atom. For the method of calculation see, for example, N. F. Mott and H. Jones, reference 3, p. 54.

[23] A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena* (McGraw Hill Co., 1932), p. 75.

[24] W. G. Burgess, Zeits. f. Physik **80**, 352 (1933).

[25] W. G. Dow, *Fundamentals of Engineering Electronics* (Wiley, 1937), p. 537.

expect the same degree of accuracy to obtain for calculations of the energy distribution of the emitted secondaries, for example. For such a calculation it is not sufficient for us to know that the *average* energy given to a secondary is E_0 and that the *average* absorption coefficient of the secondaries is γ_s; instead, we require explicit information as to the distribution in energy of the produced secondaries and the exact absorption or scattering processes for each energy. The theory is capable of giving us a definite expression for the first, but the specific processes whereby the secondaries lose energy and change direction are outside the scope of this treatment. Consequently we can only observe that the theory predicts a spread in the energies of the emitted secondaries of about the value measured and that, neglecting the effects of absorption and scattering, we would expect a maximum in the observed energy distribution at around $(E_0+E_F)-W_a$ volts. This value is considerably greater than the experimentally determined voltage. (For silver, for example, $E_0+E_F-W_a=21$ ev, whereas the maximum yield occurs for a secondary energy of only about 6 ev),[26] but of course the effect of scattering, etc., would be in this direction.

The same factors limit the accuracy of predictions as to the manner in which δ should be affected by changes in the work function. To be sure, from Eq. (47) we are justified in writing, for such a case

$$\delta_\infty \propto \frac{1-(W_a/(E_0+E_F))^{\frac{1}{2}}}{\gamma_s}.$$

Or, nearly enough

$$\delta_{\max} \propto \frac{1-(W_a/(E_0+E_F))^{\frac{1}{2}}}{\gamma_s}.$$

Since $W_a=E_{\max}+\chi$,

$$-\frac{d}{d\chi}\log_e \delta_{\max} = \frac{d}{d\chi}\log_e \gamma_s + \frac{1}{2(E_0+E_F)(W_a/(E_0+E_F))^{\frac{1}{2}} \times\{1-(W_a/(E_0+E_F))^{\frac{1}{2}}\}}. \quad (54)$$

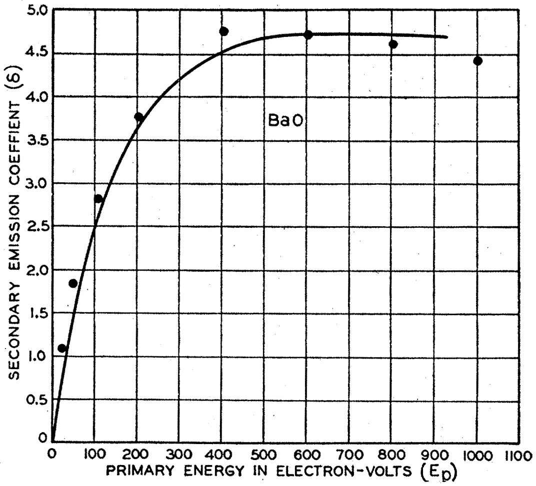

FIG. 14. Secondary yield *vs.* primary energy curve for barium oxide. Experimental points taken from Bruining and de Boer.

The second term of this expression can be evaluated, but again the first term has to do with the detailed behavior of secondaries of different energies. The average "absorption coefficient" will necessarily depend on the amount of energy a secondary must lose or the deflection it must suffer to be prevented from escaping and this, in turn, depends on χ in a manner which we cannot now predict. We can only estimate that γ_s will increase with χ at a rate whose order of magnitude should be given by some such relation as the following:

$$\gamma_s \propto \frac{1}{E_0+E_F-W_a}.$$

That is, the greater the energy that can be taken from the "average" secondary without preventing its escape, the less the "absorption coefficient." Therefore,

$$\frac{d}{d\chi}\log_e \gamma_s \sim \frac{1}{E_0+E_F-W_a}. \quad (55)$$

Now Treloar[27] has reported measurements wherein the work functions of tungsten and molybdenum were decreased by evaporating small amounts of barium or thorium on to the targets. By simultaneous measurements of χ and $\delta_{\max}$, Treloar was able to establish a linear

---

[26] E. Rudberg, Proc. Roy. Soc. **127**, 111 (1930).

[27] L. R. G. Treloar, Proc. Phys. Soc. **49**, 392 (1937).

relation between log $\delta_{\max}$ and χ, provided the amount of the contaminant was kept small (less than one atomic layer). For such tiny surface deposits it seems not unreasonable to accept Treloar's assumption that the only significant change was in the work function. If so, Eq. (54) should be applicable. For either tungsten or molybdenum the value of E_0 should be ~ 28 ev. $E_{\max}$ is not known in either case, but it will be accurate enough for this calculation to assume the value corresponding to one free electron per atom. Then, in either case, $E_{\max} \sim 5$ ev, $E_F \sim 3$ ev, while $\chi \sim 3$ ev for the targets measured. For these values, Eq. (55) gives

$$\frac{d}{d\chi} \log_e \gamma_s \sim 0.04 \text{ ev}^{-1}.$$

And therefore, from Eq. (54)

$$-\frac{d}{d\chi} \log_e \delta_{\max} \sim 0.04 \text{ ev}^{-1} + 0.07 \text{ ev}^{-1} = 0.11 \text{ ev}^{-1}.$$

Treloar's values were 0.12 ev^{-1} for tungsten and 0.14 ev^{-1} for molybdenum. The good agreement is probably fortuitous.[28]

SUMMARY

In this paper a quantum-mechanical treatment has been given, in three dimensions, of the interaction between primary electrons and the lattice electrons of a bombarded metal target. A certain dependence of the results of this calculation on the primary energy was found to exist, but not at all of the form exhibited by observed yield *vs.* bombarding energy curves. The shapes of the observed curves are attributed to the more or less demonstrable fact that the primary electrons lose so much of their energy that they can produce no more secondaries, in a distance which may be *less* than the mean free path of the much lower energy secondaries. An approximate method of calculating the δ *vs.* E_p curves is developed and shown to give reasonable agreement with experiment. The dependence of the yield on the work function of the target is also shown to be susceptible of rough calculation. The calculated dependence is small and is also in satisfactory agreement with experiment.

In general, the theory predicts that a large secondary emission coefficient ($\delta > 2$ or 3, say) can be obtained for moderate (400–800-ev) primary energies only from targets having a large lattice constant and a small Fermi energy. Caesium, for example, satisfies these conditions but in the pure state, (largely on *account* of its great atomic volume), its valence electrons must be so nearly free that the binding terms, on which secondary emission principally depends, are too small to permit appreciable yields. A complex caesium surface, on the other hand, retains a large lattice spacing and (probably) a low Fermi energy and at the same time possesses a lattice potential which deviates much more from constancy than that of the pure metal. Thus it is easy to understand why the pure alkali metals are such poor secondary emitters while complex alkali surfaces are very good emitters.

The absolute magnitude of the secondary emission coefficient cannot be closely predicted without further information concerning the lattice fields. Similarly, the energy distribution of the emitted secondaries cannot be accurately predicted without a detailed knowledge of the scattering and absorption processes which affect the low energy secondaries. In each case, however, the partial prediction given by the theory is about what one would expect to need to fit the experimental results.

In conclusion, it should be pointed out that this theory treats only secondary emission which is due to the interaction of the bombarding particles with the *valence* electrons of the target material. It is probably not possible, without further investigation, to say for sure that the contribution of the closed shells is entirely negligible. The extent of the agreement between the present theory and experimental results is good enough, however, to lend support to the view that the emission of secondary electrons is primarily due to the valence electrons, in some cases at least.

---

[28] It should be mentioned that Treloar's results have not been confirmed in some work reported since this paper was written (Edward A. Coomes, Phys. Rev. **55**, 519 (1939)).