Theory of the Production of Secondary Electrons in Solids*

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On the assumption of a simple Coulomb interaction between a primary and a lattice electron, a general formulation of the problem of the production of secondary electrons is given. The basic features of the existing theories of secondary emission are presented and discussed as different approximations of this formulation. Special attention is given to the process of production of secondaries and to the energy losses suffered by the bombarding primaries. Finally, the ratio is estimated of the number of secondary electrons emitted due to processes considered by Wooldridge and those investigated by Baroody.

I. INTRODUCTION

FROM the theoretical point of view the emission of electrons by a substance bombarded by a beam of primary electrons may be divided into two parts: the production of secondaries and the mechanism of their escape. In dealing with the process of production one may, at least for high primary energies, introduce approximations based on the assumption that the wave vector of the primary particle is large compared with the wave vector of a lattice electron. The wave vector of a secondary electron is usually not large enough to deal with the escape mechanism on a similar basis. This is one of the reasons why the quantitative aspect of the theory of secondary emission is rather incomplete. The first author to give a wave mechanical treatment of secondary emission was Fröhlich.[1] More recently his work was improved by Wooldridge.[2] According to these authors the free electron model of metals cannot lead to secondary emission when the primary beam is incident perpendicularly to the surface of the metal. The laws of conservation of momentum and energy would make it impossible for the lattice electrons to gain momentum in the direction towards the surface. Their theories are thus based entirely on the so-called Peierls' "Umklapp-Prozesse."

Rudberg and Slater[3] discussed the discrete energy losses suffered by inelastically reflected primaries on the basis of quantum mechanics. Recently Baroody[4] investigated the possibility of explaining some of the characteristic features of secondary emission on the basis of a free electron model, assuming that the escape of excited lattice electrons is caused by single or multiple scattering.

In all papers just referred to the interaction energy V between a primary electron with radius vector $\mathbf{R}$ and a lattice electron with radius vector $\mathbf{r}$ is assumed to be given by

$$V=e^2/|\mathbf{R}-\mathbf{r}|. \tag{1}$$

The validity of (1) may well be questioned. For metals, for example, a better approach may be to consider the conduction electrons together with the positive ion cores as a "plasma," thus taking into account the rather organized behavior of the system.[5] For insulators one should take into account the polarization of the medium, thus reducing (1) by a factor equal to the effective dielectric constant. In the latter case the essentials of the theory would not be affected. Notwithstanding the possible criticism with regard to the validity of (1), it will be assumed to hold in the present paper. It is our intention to present the theories referred to above as different approximations of a general formulation of the problem, focusing attention mainly on the production of secondaries and the energy losses suffered by the primary beam. Also, a comparison between the different approximations will be given, as well as an estimation of their relative importance to the theory of secondary emission.

II. THE FUNDAMENTAL PROCESS

Consider a primary electron with wave vector $\mathbf{K}$ moving in a crystal of unit volume. The energy of the primary particle is assumed to be large enough to consider it as free, so that its energy is $\hbar^2K^2/2m$ and its wave function $\exp[i(\mathbf{K}\cdot\mathbf{r})]$. The wave function of a lattice electron with wave vector $\mathbf{k}$ is represented by $\psi_\mathbf{k}(\mathbf{r})$ and is assumed to be normalized per unit volume. If there were no interaction between the two particles, the wave function of the system would be

$$u_0=e^{i(\mathbf{K}\cdot\mathbf{R})}\psi_\mathbf{k}(\mathbf{r})\exp(-iEt/\hbar), \tag{2}$$

where the total energy

$$E=E(\mathbf{k})+\hbar^2K^2/2m. \tag{3}$$

Because of the interaction, however, transitions are possible such that the lattice electron goes from state $\mathbf{k}$ to $\mathbf{k}'$ and the primary from $\mathbf{K}$ to $\mathbf{K}'$. The basic problem then consists of calculating the number of transitions per unit time $p(\mathbf{K}\mathbf{k}\rightarrow\mathbf{K}'\mathbf{k}')d\Omega'$ for which the primary electron is scattered into a solid angle $d\Omega'$ around the vector $\mathbf{K}'$ and the lattice electron is excited into $\mathbf{k}'$. Following the usual procedure, the wave

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[2] D. E. Wooldridge, Phys. Rev. **56**, 562 (1939).
[3] E. Rudberg and J. C. Slater, Phys. Rev. **50**, 150 (1936).
[4] E. M. Baroody, Phys. Rev. **78**, 780 (1950).
[5] D. Bohm and E. P. Gross, Phys. Rev. **75**, 1851 and 1864 (1949); D. Bohm and D. Pines, **80**, 903 (1950); **82**, 625 (1951); D. Pines and D. Bohm, Phys. Rev. **85**, 338 (1952); D. Pines, Phys. Rev. **85**, 931 (1952).

function representing the two electrons under consideration at a time t, may be expanded as follows,

$$u(t)=\sum_{\mathbf{k}'}\sum_{\mathbf{K}'} a_{\mathbf{k}'\mathbf{K}'}(t)e^{i(\mathbf{K}'\cdot\mathbf{R})}\psi_{\mathbf{k}'}(\mathbf{r})\exp(-iE't/\hbar), \quad (4)$$

where

$$E'=E(\mathbf{k}')+\hbar^2K'^2/2m. \quad (5)$$

Assuming the interaction is given by (1) and commences at $t=0$, one finds

$$a_{\mathbf{K}'\mathbf{k}'}(t)=\frac{1}{i\hbar}\int_0^t\int_{\mathbf{r}}\int_{\mathbf{R}} e^{i(\mathbf{K}-\mathbf{K}')\cdot\mathbf{R}}\frac{e^2}{|\mathbf{R}-\mathbf{r}|}\psi_{\mathbf{k}}(\mathbf{r})\psi_{\mathbf{k}'}{}^*(\mathbf{r}) \times\exp[-i(E-E')t/\hbar]d\mathbf{r}d\mathbf{R}dt, \quad (6)$$

where the integrations over $d\mathbf{r}$ and $d\mathbf{R}$ extend over the volume of the crystal. According to Bethe[6]

$$\int\frac{e^2}{|\mathbf{R}-\mathbf{r}|}e^{i(\mathbf{K}-\mathbf{K}')\cdot\mathbf{R}}d\mathbf{R}=\frac{4\pi e^2}{q^2}e^{i(\mathbf{q}\cdot\mathbf{r})}, \quad (7)$$

with $\mathbf{q}\equiv\mathbf{K}-\mathbf{K}'$. Substitution into (6) leads for the transition probability to

$$|a_{\mathbf{K}'\mathbf{k}'}(t)|^2=\frac{16\pi^2e^4}{q^4}\frac{2\{1-\cos(E'-E)t/\hbar\}}{(E'-E)^2}|I|^2, \quad (8)$$

with

$$I\equiv\int e^{i(\mathbf{q}\cdot\mathbf{r})}\psi_{\mathbf{k}}(\mathbf{r})\psi_{\mathbf{k}'}{}^*(\mathbf{r})d\mathbf{r}. \quad (9)$$

For large values of t expression (8) has a strong maximum for $E'-E=0$, i.e., for processes in which energy is conserved. According to standard procedure one has to integrate over a large number of final states for which the primary particle has a value in the neighborhood of $\mathbf{K}'$. Expression (8) should therefore be multiplied by the number of states with a wave vector of magnitude between K' and $K'+dK'$ within a solid angle $d\Omega'$ around $\mathbf{K}'$, i.e., by $K'^2dK'd\Omega'=mK'dE'd\Omega'/\hbar^2$, and integrated over dE'. The time derivative of the resulting expression then gives the rate $p(\mathbf{Kk}\rightarrow\mathbf{K}'\mathbf{k}')d\Omega'$ at which these transitions occur. Thus,

$$p(\mathbf{Kk}\rightarrow\mathbf{K}'\mathbf{k}')d\Omega'=(4me^4K'/\hbar^3q^4)|I|^2d\Omega'. \quad (10)$$

In what follows it is convenient to consider a beam of primary particles of density $m/\hbar K$, so that one particle crosses unit area per unit time. The rate of the transitions defined above then becomes

$$P(\mathbf{Kk}\rightarrow\mathbf{K}'\mathbf{k}')d\Omega'=(4m^2e^4K'/\hbar^4q^4K)|I|^2d\Omega'. \quad (11)$$

The various theories referred to in the introduction differ essentially only in the manner in which the integral I, given by (9), is evaluated. Assuming the lattice electrons to be free, the theory of production of secondaries should become identical with Baroody's theory. The "nearly free" approximation yields results similar to those obtained by Wooldridge. The "tightly bound" approximation is in accordance with the discussion by Rudberg and Slater and, as far as energy losses are concerned, corresponds to the theory of Bethe. The first two approximations will be discussed in the next section, the third one in Sec. IV.

[6] H. Bethe, Ann. Phys. 5, 325 (1930).

III. WEAKLY BOUND LATTICE ELECTRONS

Describing the lattice electrons by Bloch functions, we may write,

$$\psi_{\mathbf{k}}(\mathbf{r})=e^{i(\mathbf{k}\cdot\mathbf{r})}u_{\mathbf{k}}(\mathbf{r}), \quad (12)$$

where $u_{\mathbf{k}}(\mathbf{r})$, a function with the same periodicity as the lattice, may be expanded in a Fourier series,

$$u_{\mathbf{k}}(\mathbf{r})=\sum_{n_1n_2n_3=0}^{\infty}c_{\mathbf{n}}(\mathbf{k})\exp[i(\mathbf{n}\cdot\mathbf{r})],$$

with

$$\textstyle\sum_{\mathbf{n}}|c_{\mathbf{n}}(\mathbf{k})|^2=1. \quad (13)$$

Here, $\mathbf{n}/2\pi$ is a vector denoting one of the points in the reciprocal lattice. For cubic crystals with a lattice constant a, $a\mathbf{n}/2\pi$ represents a vector with integral components. For body-centered cubic crystals those coefficients are zero for which the sum of the components of $a\mathbf{n}/2\pi$ is odd. Because the absolute value of the coefficients c decreases with increasing values of n, the most important terms that do not vanish for a b.c.c. lattice are c_{000}; c_{110}, etc.; c_{200}, etc.$\cdots$. We should note, however, that if $\mathbf{k}$ is equal or nearly equal to $\mathbf{n}$, $c_{\mathbf{n}}$ is not small compared with c_{000}. For a face centered cubic lattice only those coefficients do not vanish for which all components of $a\mathbf{n}/2\pi$ are odd or even. In this case then, the coefficients not equal to zero are, in order of decreasing magnitude, c_{000}; c_{111}, etc.; c_{200}, etc. $\cdots$. For a given $\mathbf{n}$ the coefficients $c_{\mathbf{n}}(\mathbf{k})$ also increase with increasing values of k, though slowly as long as k is appreciably smaller than n. It will be assumed in what follows that the lattice electrons excited by the primary beam into states denoted by $\mathbf{k}'$ may be considered as completely free, i.e., $c_{000}(\mathbf{k}')=1$ and $c_{\mathbf{n}}(\mathbf{k}')=0$ for $\mathbf{n}\neq0$.

On the basis of this assumption, substitution of (12) and (13) into (9) leads for the matrix element to

$$I=\textstyle\sum_{\mathbf{n}}c_{\mathbf{n}}(\mathbf{k})\int\exp[i(\mathbf{q}+\mathbf{k}-\mathbf{k}'+\mathbf{n})\cdot\mathbf{r}]d\mathbf{r}. \quad (14)$$

The integral is unity if

$$\mathbf{q}+\mathbf{k}-\mathbf{k}'+\mathbf{n}=0 \quad \text{or} \quad \mathbf{K}+\mathbf{k}+\mathbf{n}\equiv\mathbf{C}_{\mathbf{n}}=\mathbf{k}'+\mathbf{K}', \quad (15)$$

and has a negligible value otherwise. (15) expresses the law of conservation of momentum of the system. For a particular value of $\mathbf{n}$ the contribution to expression (11) is given by

$$P_{\mathbf{n}}(\mathbf{Kk}\rightarrow\mathbf{K}'\mathbf{k}')d\Omega'=|c_{\mathbf{n}}(\mathbf{k})|^2(4m^2e^4K'/\hbar^4q^4K)d\Omega'. \quad (16)$$

Obviously, large values of $P_{\mathbf{n}}$ only occur for small values of q. According to the energy conservation law,

the minimum value of q is equal to

$$q_{\min}=\frac{2m}{\hbar^2}\frac{E(\mathbf{k}')-E(\mathbf{k})}{K+K'}\simeq\frac{m}{\hbar^2}\frac{E(\mathbf{k}')-E(\mathbf{k})}{K}, \quad (17)$$

which is very small for high primary energies. The approximation holds if $K\gg k$. For transitions defined by $\mathbf{n}\neq 0$, it thus follows from (15) and (16) that only those are allowed for which the excited state of the lattice electrons is determined by

$$\mathbf{k}'\simeq\mathbf{k}+\mathbf{n} \quad \text{for} \quad \mathbf{n}\neq 0, \quad (18)$$

i.e., for which the reduced wave vector does not change. For transitions defined by $\mathbf{n}=0$, (18) does not hold and (15) reduces to the "classical" momentum law

$$\mathbf{K}+\mathbf{k}=\mathbf{K}'+\mathbf{k}' \quad \text{for} \quad \mathbf{n}=0. \quad (18a)$$

Each of these types of transitions will now be discussed separately.

a. Transitions Defined by $n\neq 0$

The number of transitions $P_{\mathbf{n}}(\mathbf{k},\mathbf{k}')$ taking place per unit time from an initial state defined by $\mathbf{K}$, $\mathbf{k}$, and $\mathbf{n}$ may now be calculated from (16). The final state of the lattice electron is given immediately by (18), so that $E(\mathbf{k}')-E(\mathbf{k})$, and hence, also K', is fixed. Introducing in momentum space a polar coordinate system with $\mathbf{K}$ as z-axis and θ and ϕ as polar angles defining the orientation of $\mathbf{K}'$, one may thus write

$$q^2=K^2+K'^2-2KK'\cos\theta, \quad (19)$$

or

$$qdq=-KK'd(\cos\theta). \quad (20)$$

It follows that

$$d\Omega'=(qdq/KK')d\phi. \quad (21)$$

Substituting (21) into (16) and integrating over q from $q_{\min}=K-K'$ to $q_{\max}=K\gg q_{\min}$ one obtains

$$P_{\mathbf{n}}(\mathbf{k},\mathbf{k}')\simeq|c_{\mathbf{n}}(\mathbf{k})|^2 4\pi e^4/E_{\mathbf{k}'\mathbf{k}}^2,$$

with

$$E_{\mathbf{k}'\mathbf{k}}\equiv E(\mathbf{k}')-E(\mathbf{k}). \quad (22)$$

It should be observed that the number of these processes is independent of the energy of the primary particle, although it should be kept in mind that the derivation is based on the assumption that $K\gg k$. As a consequence of the occurrence of $E_{\mathbf{k}'\mathbf{k}}^2$ in the denominator and $|c_{\mathbf{n}}(\mathbf{k})|^2$ in the numerator, the number of processes under consideration decreases with increasing values of n. Except for a factor that is practically equal to unity, (22) is identical with Wooldridge's formula (32) in the paper referred to above.

Each transition of the kind just discussed leads to a secondary electron in a state $\mathbf{k}'=\mathbf{k}+\mathbf{n}$. Therefore, Eq. (22) describes the production of secondaries when multiplied by the number of lattice electrons initially in state $\mathbf{k}$. It may be noted that an electron with a wave vector $2\pi/a$, where $a\simeq 3A$ has an energy of about 20 ev. As k is usually appreciably smaller than n, the secondaries produced have momenta strongly determined by the direction of $\mathbf{n}$.

The influence of the direction of $\mathbf{k}$ relative to $\mathbf{n}$ on the magnitude of expression (22) may be estimated by making use of the approximation

$$E(\mathbf{k})\simeq\hbar^2k^2/2m. \quad (24)$$

In that case

$$E_{kk'}=(\hbar^2/2m)(n^2+2\mathbf{k}\cdot\mathbf{n})=(\hbar^2/2m)(n^2+2k_nn), \quad (25)$$

where k_n is the component of $\mathbf{k}$ along the direction $\mathbf{n}$. For a given vector $\mathbf{n}$ and a given value of k the transition probability is a maximum when $\mathbf{k}$ has the opposite direction of $\mathbf{n}$ and a minimum for $\mathbf{k}$ and $\mathbf{n}$ parallel.

According to (25) the energy lost by the primary particle because of a transition of the lattice electron from $\mathbf{k}$ to $\mathbf{k}+\mathbf{n}$ only depends on n^2 and on k_n. Thus, for a given vector $\mathbf{n}$ all those lattice electrons for which the component of $\mathbf{k}$ along $\mathbf{n}$ has a value between k_n and k_n+dk_n will gain energy between $E_{kk'}$ and $E_{kk'}+dE_{kk'}$ where $E_{kk'}$ is given by (25). Denoting the number in this group by $N(E_{kk'})dE_{kk'}$, the distribution of energy losses is given by

$$P_{n\ \text{total}}(E_{kk'})dE_{kk'}=v_n\langle|c_n(k)|^2\rangle_{\text{Av}}\frac{4\pi e^4}{E_{kk'}^2}N(E_{kk'})dE_{kk'}. \quad (26)$$

In this expression v_n denotes the number of vectors $\mathbf{n}$ that have the same absolute value n. The coefficient $\langle|c_n(k)|^2\rangle_{\text{Av}}$ represents a suitable average to take into account the fact that not all lattice electrons in the group $N(E_{kk'})dE_{kk'}$ have the same coefficient $c_{\mathbf{n}}(\mathbf{k})$. Clearly, $\langle|c_n(k)|^2\rangle_{\text{Av}}$ depends on k_n and therefore on $E_{kk'}$, though not strongly. For a "Fermi sphere" with maximum wave vector k_m, the number of electrons in the group dk_n defined above would be equal to $(k_m^2-k_n^2)dk_n/4\pi^2$. Hence, only for $k_n\ll k_m$ would $N(E_{kk'})$ be nearly constant.

The total energy loss of the primary beam caused by transitions defined by a specific value of n may be roughly estimated by observing that the value of $E_{kk'}$ given by (25) averaged over all electrons with the same initial value of k is equal to $\hbar^2n^2/2m=E_0$, and hence, independent of k. Together with (26) this leads to the following contribution to the energy loss of the primary beam per unit path

$$-\left(\frac{dE_p}{dx}\right)_n=\frac{8\pi e^4Nm}{\hbar^2n^2}v_n\langle|c_n(k)|^2\rangle_{\text{Av}}=\frac{4\pi e^4N}{E_0}v_n\langle|c_n(k)|^2\rangle_{\text{Av}}. \quad (27)$$

This expression is again independent of the energy of the primary particles. It should be noted, however,

that by using the average value E_0, the higher probability of small energy losses has not been taken into account, so that (27) is only a rough approximation. Similarly, the production of secondaries as determined by (22) may be approximated by

$$P_n(k')\simeq(4\pi e^4N/E_0^2)v_n\langle|c_n(k)|^2\rangle_{\text{Av.}} \tag{22a}$$

b. Transitions Defined by $n=0$

This case corresponds to transitions of completely free electrons, i.e., to a Sommerfeld model of a metal. Because of the momentum law (18a) and the energy conservation law, the lattice electrons mainly gain momentum in a direction perpendicular to the wave vector $\mathbf{K}$ of the primary particle. In other words, when $\mathbf{K}$ is directed perpendicularly away from the surface, the lattice electrons mainly gain momentum parallel to the surface. This led Fröhlich and Wooldridge to believe that transitions of this type are unimportant for the process of secondary emission. However, as assumed by Baroody, electrons that have gained momentum parallel to the surface may still be able to escape by scattering processes. The scattering may be caused by impurities or by lattice vibrations. In both cases, the periodicity of the lattice is disturbed, but in the latter case the cross section for scattering is temperature dependent. Besides, of course, the excited lattice electrons will interact with the other free electrons, thus leading to absorption of the secondaries during their escape. Also, the primary electrons, even though they may impinge perpendicularly on the surface, will be subject to Rutherford scattering inside the metal and their path will be curved rather than linear. This is born out by experiments with high primary energies, whereby an appreciable percentage of primaries has been observed to leave the metal again at the surface of incidence after having lost a certain amount of energy. Therefore, even without scattering of the secondaries it should be possible to obtain secondary emission with a free electron model. *A priori* it is not at all obvious that the case $\mathbf{n}=0$ should not enter into a discussion of secondary emission.

To discuss these transitions Eq. (16) will again be used as a starting point, but with a transformation of $d\Omega'$ different from (21) as used for $\mathbf{n}\neq0$. Suppose the wave vectors of the primary electron and a lattice electron are given. Then the momentum law requires $\mathbf{K}+\mathbf{k}\equiv\mathbf{C}_0=\mathbf{K}'+\mathbf{k}'$. Because of the energy law, $(K'^2+k'^2)$ is also determined by the initial state. Introducing a polar coordinate system with $\mathbf{C}_0$ as z-axis and the angles θ and ϕ to define the direction of $\mathbf{K}'$ one may thus write

$$k'^2=K'^2+C_0^2-2C_0K'\cos\theta, \tag{28}$$

and by differentiation of both sides

$$-d(\cos\theta)=\frac{k'dk'}{K'}\left(\frac{2}{C_0}-\frac{\cos\theta}{K'}\right)\simeq\frac{k'dk'}{KK'}, \tag{29}$$

so that $d\Omega'$ may be expressed in the variables k' and ϕ,

$$d\Omega'\simeq(k'dk'/KK')d\phi. \tag{30}$$

The approximation is valid as long as $K\gg k$. Substitution of (30) into (16) thus leads for the number of transitions per unit time whereby the lattice electron, initially in state $\mathbf{k}$, is scattered into a state between k' and $k'+dk'$ to

$$P_0(k')dk'=\frac{4m^2e^4k'dk'}{\hbar^4K^2}\int_0^{2\pi}\frac{d\phi}{|\mathbf{k}'-\mathbf{k}|^4}, \tag{31}$$

(the coefficient $c_0(\mathbf{k})$ has been put equal to unity). In case $k'\gg k$, the integral is simply $2\pi/k'^4$. This condition is equivalent to the assumption $\mathbf{k}=0$, used by Baroody to calculate the momentum transferred from the primary to the lattice electron. For N free electrons per unit volume, this assumption leads for the total number of lattice electrons scattered into states between k' and $k'+dk'$, per unit time, to

$$P_{0\text{ total}}(k')dk'=(8\pi m^2e^4N/\hbar^4K^2)dk'/k'^3$$
$$=(\pi e^4N/E_p)dE_{k'}/E_{k'}^2, \tag{31a}$$

there E_p represents the primary energy and $E_{k'}$ the energy loss involved in any one of these transitions.

In general, however, the assumption $k'\gg k$ is not allowed because transitions for which $|\mathbf{k}'-\mathbf{k}|$ is small are more frequent than those for which this quantity is large. More accurate results are therefore obtained as follows: multiply (31) by the number of lattice electrons that may be scattered into states $\mathbf{k}'$ by an increase of momentum $\hbar|\mathbf{k}'-\mathbf{k}|$. If α is the angle between $\mathbf{k}$ and $\mathbf{k}'$, this number is equal to $k^2dk\sin\alpha d\alpha/2\pi^2$. Integration of the resulting expression over α and ϕ then yields

$$P_{0\text{ total}}(k')dk'=\frac{8m^2e^4}{\pi\hbar^4K^2}k'dk'\int_0^{k_m}\frac{k^2dk}{(k'^2-k^2)^2}, \tag{32}$$

where the upper limit k_m corresponds to the wave vector of an electron at the top of the Fermi distribution. Integration over k gives

$$P_{0\text{ total}}(k')dk'$$
$$=\frac{2me^4}{\pi\hbar^2E_p}k'dk'\left[\frac{k_m}{k'^2-k_m^2}-\frac{1}{2k'}\log\left(\frac{k'+k_m}{k'-k_m}\right)\right]. \tag{31b}$$

This expression reduces to (31a) by making a series expansion in terms of k_m/k' and retaining only the terms of lowest order in this variable, and finally putting $k_m^3=3\pi^2N$.

The distribution of energy losses may be obtained from (32) by introducing $E_{kk'}=\hbar^2(k'^2-k^2)/2m$ as variable instead of k', and integrating over k. Thus

$$P_{0\text{ total}}(E_{kk'})dE_{kk'}=\frac{\pi e^4N}{E_p}\frac{dE_{kk'}}{E_{kk'}^2}\quad\text{for}\quad E_{kk'}>E_m, \tag{33a}$$

$$=\frac{\pi e^4N}{E_p}\left[1-\left(1-\frac{E_{kk'}}{E_m}\right)^{\frac{3}{2}}\right]\frac{dE_{kk'}}{E_{kk'}^2}\quad\text{for}\quad E_{kk'}<E_m. \tag{33b}$$

The difference between these two expressions is caused by the fact that in the later case only those lattice electrons can contribute for which

$$k_m(1-E_{kk'}/E_m)^{\frac{1}{2}}<k<k_m,$$

because k' must be larger than k_m in view of the exclusion principle. For $E_{kk'}\ll E_m$ Eq. (33b) varies as $1/E_{kk'}$.

The total energy loss per unit primary path length is obtained by multiplying (33a) and (33b) by $E_{kk'}$ and integrating from zero to E_p. This yields

$$-(dE_p/dx)_{n=0} = (\pi e^4 N/E_p)[8/3-\log 4+\log(E_p/E_m)]. \quad (34)$$

To compare this result with that obtained in the next section for strongly bound electrons, it is convenient to write it as

$$-(dE_p/dx)_{n=0}=(\pi e^4 N/E_p)\log(2E_p/E_i), \quad (34a)$$

with $E_i=8E_m e^{-8/3}=0.55E_m$.

IV. THE APPROXIMATION OF STRONGLY BOUND ELECTRONS

For strongly bound electrons the wave functions are nearly identical with the atomic wave functions. In other words, the wave function of an electron strongly bound to an atom located at a lattice point defined by a vector $\mathbf{r}_i$, has appreciable value only in the vicinity $|\mathbf{r}-\mathbf{r}_i|$ of the order of the atomic radius. Also, according to (11) only transitions for which q is closely equal to $q_{\min}$ have appreciable probability of occurrence. For usual primary energies of some hundreds of volts, $q_{\min}$ is small compared with the reciprocal interatomic distance. Thus, the factor $e^{i(\mathbf{q}\cdot\mathbf{r})}$ appearing in the integral I given by (9) may be written in good approximation as

$$e^{i(\mathbf{q}\cdot\mathbf{r})}=[1+i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}_i)]e^{i(\mathbf{q}\cdot\mathbf{r}_i)}. \quad (35)$$

Making use of the orthogonality of $\psi_{\mathbf{k}}(\mathbf{r})$ and $\psi_{\mathbf{k}'}(\mathbf{r})$, this leads to

$$|I|^2=\left|\int\{\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}_i)\}\psi_{\mathbf{k}}(\mathbf{r})\psi_{\mathbf{k}'}{}^*(\mathbf{r})d\mathbf{r}\right|^2=q^2|L_{\mathbf{kk}'}|^2 \quad (36)$$

where $|L_{\mathbf{kk}'}|^2$ is the optical transition probability. It is zero unless the reduced wave vector before and after the transition is the same, i.e., the selection rule is the same here as for the weakly bound approximation in Sec. IIIa.

The number of transitions $P(\mathbf{kk}')$ of a lattice electron from an initial state $\mathbf{k}$ to a final state $\mathbf{k}'$, per unit time, may then be found by substituting (36) into (11); introducing q and ϕ as new variables by means of the transformation (21) and integrating over q and ϕ one obtains

$$P(\mathbf{kk}')=\frac{4\pi me^4}{\hbar^2E_p}|L_{\mathbf{kk}'}|^2\log\frac{q_{\max}}{q_{\min}}.$$

The limits are the same as before, i.e., $q_{\min}=K-K'=mE_{kk'}/\hbar^2K$ and $q_{\max}=K$. Thus,

$$P(\mathbf{kk}')=\frac{4\pi me^4}{\hbar^2E_p}|L_{\mathbf{kk}'}|^2\log\frac{2E_p}{E_{kk'}}=\frac{2\pi e^4}{E_p}\frac{f_{\mathbf{kk}'}}{E_{kk'}}\log\frac{2E_p}{E_{kk'}}, \quad (37)$$

where

$$f_{\mathbf{kk}'}=\frac{2m}{\hbar^2}E_{kk'}|L_{\mathbf{kk}'}|^2. \quad (38)$$

Expression (37) governs the production of secondaries into states with a prescribed wave vector $\mathbf{k}'$. For the distribution of energy losses suffered by the primary particles it follows immediately that

$$P(E_{kk'})dE_{kk'}=\text{const.}f_{\mathbf{kk}'}N(E_{kk'})dE_{kk'}/E_{kk'}, \quad (39)$$

where $N(E_{kk'})dE_{kk'}$ represents the number of transitions that give rise to an energy loss in the defined range.

The energy loss per unit primary path length caused by the interaction with a single lattice electron making transitions from $\mathbf{k}$ to $\mathbf{k}'$ is given by expression (37) multiplied by $E_{kk'}$. The total energy loss per unit path caused by a single atom is thus obtained by summation over all initial states $\mathbf{k}$ and all final states $\mathbf{k}'$. If there are N_a atoms per unit volume the total energy loss of the primary beam per unit path is thus given by

$$-\left(\frac{dE_p}{dx}\right)=\frac{2\pi e^4}{E_p}N_a\sum_{\mathbf{k}'}\sum_{\mathbf{k}}f_{\mathbf{kk}'}\log\frac{2E_p}{E_{kk'}}, \quad (40)$$

an expression identical with Bethe's formula (66) in the paper referred to above. Now, for an atom the oscillator strength summed over all initial and final states is equal to the number of electrons Z. When the primary energy is larger than the binding energy of an electron in the K-shell all electrons take part in the absorption process. For smaller primary energies, less than Z, say Z' electrons contribute to the loss of energy of the primaries. Introducing an average energy E_i' defined by

$$Z'\log E_i'=\sum_{\mathbf{k}'}\sum_{\mathbf{k}}f_{\mathbf{kk}'}\log E_{kk'}, \quad (41)$$

wherein the summation over $\mathbf{k}$ includes all initial states taking part in the absorption process, (40) may be written as,

$$-(dE_p/dx)=(2\pi e^4/E_p)N_aZ'\log(2E_p/E_i'). \quad (40a)$$

From what has been said above it follows that E_i' is a slowly varying function of E_p.

V. CONCLUDING REMARKS

Each particular one of the approximations dealt with above should apply to those energy bands for which the approximation is most fitting. However, a certain amount of overlapping of the cases $\mathbf{n}=0$ and $\mathbf{n}\neq 0$ on the one hand and, of $\mathbf{n}\neq 0$ and the tightly bound electron approximation on the other, can hardly be avoided. The approximation of completely free electrons would be expected to hold reasonably well for the

valence electrons of the alkali metals, whereas for the valence electrons of other metals a combination of $\mathbf{n}=0$ and $\mathbf{n}\neq 0$, i.e., of Baroody's and Wooldridge's theories, is probably more suitable. The contribution of the innermost electronic shells to the production of secondaries and to the energy losses suffered by the primaries is probably best described by the strongly bound approximation.

It is interesting to note that both the free electron model and the strongly bound approximation lead for the energy losses of the primaries per unit path to the same dependence on E_p, *viz.*, $E_p^{-1}\log E_p$. The only difference between (34a) and (40a) is the occurrence of a factor 2 in the latter. That this factor does not occur in (34a) is a consequence of the free electron approximation.[7] Formula (27) for the case $\mathbf{n}\neq 0$, although a rough approximation, shows that the energy loss per unit path is independent of the primary energy, so that the range of the primaries would be proportional to E_p. The only case where this has been observed in the literature, to the knowledge of the authors, is in experiments by Copeland[8] on the maximum depth of origin of the secondaries in platinum films on aluminum. Copeland found the maximum depth to be proportional to E_p below 500 ev and reports this to be in agreement with Wooldridge's theory. Above 500 ev the depth of origin of the secondaries increased more rapidly, indicating a decrease of dE_p/dx with increasing values of E_p.

The distribution of energy losses, expressed by formulas (26), (33a, b), and (39) for the three approximations will be discussed with reference to experimental results in a forthcoming paper by one of us (A.v.d.Z.).

As an application to secondary emission, a rough comparison will now be made between the relative importance of the cases $\mathbf{n}=0$ and $\mathbf{n}\neq 0$ when applied to the valence electrons of copper. As no quantitative theory of the escape mechanism exists as yet, the following simplifying assumptions will be made:

(a) The secondaries are distributed isotropically when leaving the metal. This implies a polycrystalline target or a process of scattering for a single crystal target.

(b) The absorption of secondaries affects both cases in the same manner, so that in a comparison it may be neglected.

(c) Production of tertiaries by secondary electrons is neglected. On the basis of these assumptions, the secondary emission current is

$$\int_{k_1}^{K} P(k')g(k')dk', \tag{42}$$

where $g(k')$ is the probability of escape of a secondary electron with wave vector k' and $P(k')dk'$ is the number of secondaries produced per unit time per unit volume in a given range. $P(k')dk'$ is different for the two cases, but $g(k')$ is the same. Assuming k_1 is the minimum component of $\mathbf{k}'$ perpendicular to the metal surface required to escape, one may write,

$$g(k')=\tfrac{1}{2}(1-k_1/k') \quad \text{for} \quad k'>k_1, \tag{43}$$

whereas $g(k')=0$ for $k'<k_1$.

For transitions defined by $\mathbf{n}=0$, $P_0(k')dk'$ is given by expression (31b). Upon substitution into (42) and replacement of the upper limit K by ∞, integration leads to

$$I_0=\frac{\pi e^4 N}{6E_1E_p}\left[1+\left(\frac{3}{5}\right)^2\left(\frac{E_m}{E_1}\right)+\left(\frac{3}{7}\right)^2\left(\frac{E_m}{E_1}\right)^2+\left(\frac{3}{9}\right)^2\left(\frac{E_m}{E_1}\right)^3+\cdots\right], \tag{44}$$

where $E_1=\hbar^2k_1^2/2m$. For transitions defined by a given value of n, the production of secondaries is given approximately by (22a). As each of the secondaries has an energy $E_0=\hbar^2n^2/2m$, (42) becomes for $\mathbf{n}\neq 0$

$$I_n=v_n\langle|c_n(k)|^2\rangle_{\mathrm{Av}}(2\pi e^4N/E_0^2)\{1-(E_1/E_0)^{\frac{1}{2}}\}. \tag{45}$$

Inasmuch as the latter expression is independent of the primary energy, the relative importance of the two cases may be estimated by calculating the value of E_p for which (44) and (45) become equal. For energies below this value (44) is predominant, for higher energies (45) is predominant. Taking Cu as an example, with the following values as given by Wooldridge: $v_n=8$ (f.c.c. lattice), $E_m=7$ ev, $E_1=12$ ev, $E_0=35$ ev, $(c_{111})^2\simeq 0.01$, one finds that (44) and (45) become equal for $E_p\simeq 300$ ev.

The energy loss of the primary electrons per unit path may also be compared for the two cases, by making use of (34a) and (27). For Cu these expressions become equal for $E_p\simeq 600$ ev. This is appreciably larger than the primary energy for which the secondary emission currents are equal, as calculated above. The reason for this difference is apparently that the secondaries produced by transitions of the type $\mathbf{n}=0$ have less energy than those produced by transitions $\mathbf{n}\neq 0$. Consequently, the probability of escape of the former is smaller and although the value of dE_p/dx for $E_p=300$ ev is larger for the free electron case, $I_0<I_n$.

From what has been said above it seems justified to conclude that for metals bombarded by primaries of several hundred volts, a combination of the theories of Baroody and Wooldridge is necessary. The range of predominance of each of these approximations will depend on the particular target under consideration. It would be interesting to investigate experimentally the angular distribution of the secondaries emitted by single crystals. In this way, some more pertinent information about the scattering process during the escape might be obtained.

[7] See also N. F. Mott and H. S. W. Massey, *Atomic Collisions* (Oxford University Press, London, England, 1949), second edition, p. 252.

[8] P. L. Copeland, Phys. Rev. **58**, 604 (1940).