PHYSICAL REVIEW VOLUME 101, NUMBER 6 MARCH 15, 1956

Excitation of Electrons in Metals by Primary Electrons*

E. M. Baroody
Battelle Memorial Institute, Columbus, Ohio

(Received September 29, 1955)

The excitation of conduction electrons represented by Bloch wave functions through Coulomb interaction with a medium-fast primary is discussed. It is brought out that when the excitation energy is much smaller than the primary energy, the probabilities of transitions in which momentum is exchanged with the lattice (umklapp processes) are proportional to the corresponding probabilities for excitation by light (as was shown by Rudberg and Slater), and that the excitation rate varies roughly as the reciprocal of the primary energy. For cubic metals, the number of transitions per unit primary path with excitation energy in a differential range near $\epsilon = h\nu$ proves to be a simple factor multiplied by the photoelectric absorbing power for light of frequency ν. Using this relationship, and accepting Butcher's interpretation of their optical properties, a rather detailed picture is obtained of the umklapp processes which might be of importance for secondary emission from several alkali metals. The contribution of such transitions appears to be small, but not entirely negligible, in comparison with what would be expected from a free-electron gas. Some remarks are made on the possibility that innershell electrons make an important contribution to secondary emission.

1. INTRODUCTION

WHEN an electron with energy in the range several hundred to several thousand electron volts traverses a metal, a significant part of the energy which it loses is transferred to the conduction electrons. Although numerous papers have appeared which have a bearing on this process, workers interested in secondary electron emission long gave special attention to those of Fröhlich[1] and Wooldridge,[2] regarding the second paper as an extension and correction of the first. Both authors described the metal electrons by Bloch wave functions, treated the effect of the primary by perturbation theory, and placed great emphasis on those transitions in which the interacting pair of electrons exchange momentum with the lattice as a whole. In such transitions, sometimes referred to as "umklapp processes," the unreduced wave vector **k** of the metal electron may change by a large amount even though the wave vector change of the primary is extremely small. The major difference between the results of the two papers concerned the dependence of the number of such transitions per unit primary path upon the primary energy, Wooldridge finding very little dependence on primary energy for a substantial range of energies. Actually, this result is a consequence of an erroneous approximation which was introduced by Wooldridge. This fact, overlooked for a long time, was noticed independently by Marshall[3] and Baroody[4] in 1952, but no adequate discussion of the point was published at that time. When the error is corrected, the status of the umklapp processes is substantially altered. The transitions per unit primary path are roughly proportional to the reciprocal of the primary energy, and the close relationship between excitation by electrons and by light, which had been obscured before, becomes prominent. One is, in fact brought back to earlier results, particularly to those of Rudberg and Slater[5] who emphasized that the transition probabilities which they calculated became proportional to optical transition probabilities when the energy of the incident electron was large compared to the excitation energy.

The present paper is mainly devoted to a treatment of the most probable umklapp processes, including a calculation of their distribution in energy. The work was guided in part by discussions of the absorption of light, particularly those of Fan[6] and Butcher,[7] and leads to a relationship which yields considerable information about the place of umklapp processes in electron scattering from experimental data on optical properties. As derived here, the relationship depends upon the use of one-electron wave functions of the Bloch form for the metal electrons, but does not require further assumptions concerning these wave functions. In an earlier version of the work,[8] essentially the same relationship was derived using the approximation of nearly free electrons.

Because of their simplicity, and because their optical properties are better understood than those of other metals, the theory is applied to several of the alkalis. The last section of the paper considers the relative importance of various types of excitation for secondary emission. It compares the number of umklapp processes involving excitation to the second Brillouin zone with a rough estimate of the number of transitions to the same energy range which would be expected if the conduction electrons were completely free, and also calls attention to the need for more information about the excitation of innershell electrons.

---

* This work was supported by the U. S. Army Signal Corps and the U. S. Air Force.

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

[2] D. E. Wooldridge, Phys. Rev. 56, 562 (1939).

[3] J. F. Marshall, Phys. Rev. 88, 416 (1952).

[4] E. M. Baroody, Phys. Rev. 89, 910 (1953).

[5] E. Rudberg and J. C. Slater, Phys. Rev. 50, 150 (1936).

[6] H. Y. Fan, Phys. Rev. 68, 43 (1945).

[7] P. N. Butcher, Proc. Phys. Soc. (London) A64, 765 (1951).

[8] E. M. Baroody, Phys. Rev. 96, 837 (1954).

Before turning to the calculations, it must be emphasized that the paper is limited to the one-electron approximation in which the incident electron interacts with individual metal electrons through an unscreened Coulomb field. A clear understanding of the implications of this type theory appears to be indispensable, even though an entirely satisfactory treatment may require taking into account the collective description of electron interactions which has been developed by Bohm, Pines, and others.[9]

2. DEPENDENCE OF EXCITATION RATE UPON THE MOMENTUM CHANGE OF THE PRIMARY

The excitations to be considered involve the transfer of a few electron volts to a conduction electron from a relatively fast primary, and will be regarded as caused by an unscreened Coulomb interaction between the two electrons. The initial state of the interacting electrons may be described by the following wave function:

$$\exp(i\mathbf{K}\cdot\mathbf{R})u_{\mathbf{k}}(\mathbf{r})\exp(i\mathbf{k}\cdot\mathbf{r}).$$

The first factor is a plane wave, normalized to represent one incident electron per unit volume, or a current density $\hbar K/m$. The remaining factors constitute $\psi_{\mathbf{k}}(\mathbf{r})$, the Bloch wave function for an electron of energy $E(\mathbf{k})$, and it is understood that this function is also normalized for unit volume. As a result of the interaction, there is a certain probability per unit distance along its path that the incident electron will make a transition to a new state of wave vector $\mathbf{K}'$, lying in the solid angle $d\Omega'$, a metal electron simultaneously jumping from $\mathbf{k}$ to $\mathbf{k}'$. The perturbation calculation leading to this quantity has been summarized by Dekker and van der Ziel.[10] It will be sufficient here to state the result:

$$P(\mathbf{Kk}\rightarrow\mathbf{K}'\mathbf{k}')d\Omega'=(4m^2e^4K'/\hbar^4q^4K)|I|^2d\Omega', \qquad (1)$$

where[11] $\mathbf{q}=\mathbf{K}-\mathbf{K}'$ is the change in the wave vector of the primary electron, and

$$I=\int\psi_{\mathbf{k}}\psi_{\mathbf{k}'}^*\exp(i\mathbf{q}\cdot\mathbf{r})d\mathbf{r}. \qquad (2)$$

The integral is over unit volume and it is understood that the energy law,

$$E(\mathbf{k}')=E(\mathbf{k})+(\hbar^2/2m)(K^2-K'^2), \qquad (3)$$

is satisfied.

Because they are solutions of the Schrödinger equation for a periodic potential, the wave functions $\psi_{\mathbf{k}}(\mathbf{r})$ satisfy the relation

$$\psi_{\mathbf{k}}(\mathbf{r}+\mathbf{G})=\psi_{\mathbf{k}}(\mathbf{r})\exp(i\mathbf{k}\cdot\mathbf{G}), \qquad (4)$$

where $\mathbf{G}$ is a lattice vector. Inserting Eq. (4) into Eq. (2), one obtains the following:

$$I=I_0\sum\nolimits_{\mathbf{G}}\exp[i(\mathbf{k}-\mathbf{k}'+\mathbf{q})\cdot\mathbf{G}]. \qquad (5)$$

Here I_0 is the integral of Eq. (2) extended over the unit cell at the origin. A nonvanishing transition probability is obtained only when the terms in the sum over the lattice points are in phase. That is, one must have

$$\mathbf{k}'=\mathbf{k}+\mathbf{q}+2\pi\mathbf{H}, \qquad (6)$$

where $\mathbf{H}$ is a reciprocal lattice vector. When this selection rule is satisfied, the sum is just N, the number of cells per unit volume.

For transitions with $\mathbf{H}=0$ (ordinary transitions), the integral may be obtained at once in either of two special cases. If the electrons are free, so that $\psi_{\mathbf{k}}=\exp(i\mathbf{k}\cdot\mathbf{r})$, one obtains $I=1$ for all values of $\mathbf{q}$. On the other hand, if the departure of $\psi_{\mathbf{k}}(\mathbf{r})$ from a plane wave is large, one still obtains $I=1$, provided $\mathbf{q}$ is small compared to $\mathbf{k}$. These are, of course, familiar results and it is well known that they lead to a contribution to primary energy loss which varies roughly as the reciprocal of the primary energy.

Transitions with $\mathbf{H}\neq0$ (umklapp processes) arise only because the functions $\psi_{\mathbf{k}}(\mathbf{r})$ are not plane waves, and very little is known about $I=NI_0$ for general values of $\mathbf{q}$. In the case of small $\mathbf{q}$, adequate information is not obtained by simply placing $\mathbf{q}=0$ in the integral I_0. Because of the orthogonality of the wave functions, this would simply give $I_0=0$. However, since the integral is over a unit cell, one may obtain a useful higher approximation provided $q/2\pi$ is small compared to the smallest nonvanishing vector of the reciprocal lattice.[12] One may then use the approximation $\exp(i\mathbf{q}\cdot\mathbf{r})=1+i\mathbf{q}\cdot\mathbf{r}$, obtaining the following:

$$I_0=i\mathbf{q}\cdot\int\mathbf{r}\psi_{\mathbf{k}}\psi_{\mathbf{k}+2\pi\mathbf{H}}^*d\mathbf{r}. \qquad (7)$$

It is important to notice that no special assumption about $\psi_{\mathbf{k}}(\mathbf{r})$ is required here. The approximation applies

---

[9] Understanding of electron interactions in metals has been greatly enriched by theories which treat the metal as a plasma, and studies of their bearing on the excitation of valence electrons by relatively fast incident electrons are of considerable value. However, the significance of calculations using specific modifications of the Coulomb interaction is not clear at present. For example, J. Neufeld and R. H. Ritchie [Phys. Rev. **98**, 1632 (1955)] have concluded that a screening formula of the Debye type is not applicable when the velocity of the incident electron is large compared to the root mean square velocity of the plasma electrons, and have questioned the application of a potential of this type to the excitation of secondary electrons. A similar objection has been made by H. Fröhlich [Proc. Phys. Soc. (London) **B68**, 657 (1955)], who states that the use of a screening radius which is independent of energy is wrong for the range 50 ev to 1000 ev.

This work of Fröhlich has an important bearing on the present paper, since, using a quite different approach, he also develops a relation between effects produced by primary electrons and by light. However, the very recent date of Fröhlich's paper, and the number of questions requiring examination, make a discussion of the connections between the two papers impracticable at this time.

[10] A. J. Dekker and A. van der Ziel, Phys. Rev. **86**, 755 (1952). Van der Ziel has also considered the generalization of Eq. (1) which applies for a screened Coulomb interaction [Phys. Rev. **92**, 35 (1953)].

[11] In references 2 and 3 this vector is denoted by **S**.

[12] The conditions under which specific knowledge of I_0 is needed only for such small q are discussed after Eq. (14).

when the electrons are nearly free, as well as when they are tightly bound.

When Eq. (7) is used in Eq. (1), one obtains a transition probability per unit solid angle which is proportional to q^{-2}, whereas the Wooldridge method led to q^{-4}. A brief comment on the source of this discrepancy will suffice, since this aspect of the problem was emphasized by Marshall. Wooldridge expressed the factor $u_{\mathbf{k}}(\mathbf{r})$ of the Bloch wave function as a Fourier expansion with coefficients $a_{\mathbf{m}}(\mathbf{k})$, where (for a cubic crystal) $\mathbf{m}$ is a vector whose components are integers. He then obtained a transition probability proportional to q^{-4} multiplied by the square of a double sum involving products of the type $a_{\mathbf{m}}(\mathbf{k})a_{\mathbf{n}}^*(\mathbf{k}')$. In dealing with the sum, he considered only a few terms and gave no emphasis to the dependence of the coefficients $a_{\mathbf{n}}(\mathbf{k}')$ on $\mathbf{k}'$ and therefore on $\mathbf{q}$. When one proceeds in this way, it is easy to overlook the consequences of the orthogonality of the wave functions, and treat the sum as though it approaches a finite limit as q approaches zero. Finally, it should be noticed that the distinction between the cases $\mathbf{H}=0$ and $\mathbf{H}\neq 0$ which appeared above is not that suggested by Marshall in the next to last paragraph of reference 3. One may be interested in q near zero in either case, but is led to an integral of the product of orthogonal functions only in the second case.

3. VARIATION OF EXCITATION RATE WITH PRIMARY ENERGY

We next consider the integral of Eq. (1) over solid angle for the case $\mathbf{H}\neq 0$. Letting θ denote the angle between $\mathbf{K}'$ and $\mathbf{K}$, one has

$$q^2-(K-K')^2=2KK'(1-\cos\theta)\approx K^2\theta^2, \tag{8}$$

where the approximation holds for the numerous collisions in which θ is very small. On the other hand, from Eq. (3) one may obtain

$$(K-K')=(m\epsilon/K\hbar^2)(1+\eta)\approx K\epsilon/2E_p, \tag{9}$$

where $E_p=\hbar^2K^2/2m$ is the primary energy,

$$\epsilon=E(\mathbf{k}+2\pi\mathbf{H})-E(\mathbf{k}), \tag{10}$$

and η, which is of the order $q/\pi H$, is neglected in the final expression. Thus, to the same approximation as Eq. (7), one has

$$K^2\theta^2=q^2-q_{\min}^2, \tag{11}$$

where

$$q_{\min}=(m\epsilon^2/2E_p\hbar^2)^{\frac{1}{2}}=0.26\epsilon/E_p^{\frac{1}{2}}, \tag{12}$$

energies being in electron volts and distances in angstroms. Using Eq. (11), one obtains the following approximation for the element of solid angle:

$$d\Omega'=qdqd\phi/K^2. \tag{13}$$

Using Eqs. (13) and (7) in Eq. (1), one finds

$$Pd\Omega'\propto|I_0|^2dq/E_pq^3\propto dq/E_pq. \tag{14}$$

From Eq. (12) one sees that there will be a range of q to which Eq. (14) applies, provided

$$E_p^{\frac{1}{2}}\gg 0.26\epsilon/\pi H. \tag{15}$$

For the small $\mathbf{H}$ which are of interest here, $\pi H\sim 1$ A^{-1}, and (as will be discussed later) the bulk of the transitions correspond to $\epsilon<10$ ev. Thus, for $E_p>500$ ev, Eq. (14) may be applied when q is near its minimum. Although little is known about I_0 when q is not small, it presumably reaches a maximum for $q\sim\pi H\sim(q_{\min}K)^{\frac{1}{2}}$. Thus, a reasonable approximation to the integral over angle may be obtained by using Eq. (14) up to $q=(q_{\min}K)^{\frac{1}{2}}$, and neglecting the small contributions from larger values of q. In this way one finds

$$\int Pd\Omega'\propto E_p^{-1}\ln(q_{\max}/q_{\min})=\tfrac{1}{2}E_p^{-1}\ln(2E_p/\epsilon). \tag{16}$$

This evaluation is quite rough, but gives an essentially correct view of the dependence upon primary energy, and shows that the number of transitions per unit primary path varies approximately as the reciprocal of the primary energy. This result may be contrasted with that which would follow if it were true that I_0 approached a nonzero value as q approached zero. In that case $\int|I_0|^2q^{-3}dq$ would have been proportional to $q_{\min}^{-2}$, or proportional to E_p. The transition rate would then have been independent of the primary energy, as was found by Wooldridge.

4. DETAILED CALCULATION OF THE EXCITATION RATE

In this section, the transitions with $\mathbf{H}\neq 0$ will be considered in more detail, an expression $Q(\epsilon)$ being derived which is defined so that $Q(\epsilon)d\epsilon$ is the number of transitions with excitation energy in the range $d\epsilon$ near ϵ. For this study it is convenient to postpone the assumption that q is small, and begin with

$$I_0=\int\psi_{\mathbf{k}}\psi_{\mathbf{k}'}^*\exp(i\mathbf{q}\cdot\mathbf{r})d\mathbf{r}, \tag{17}$$

where $\mathbf{k}'=\mathbf{k}+\mathbf{q}+2\pi\mathbf{H}$, and integration is over a unit cell. Since $\psi_{\mathbf{k}}$ and $\psi_{\mathbf{k}'}$ are solutions of the same wave equation, Eq. (17) may be transformed to

$$I_0=\frac{\hbar i}{E(\mathbf{k}')-E(\mathbf{k})}\int(\mathrm{div}\mathbf{j})\exp(i\mathbf{q}\cdot\mathbf{r})d\mathbf{r}, \tag{18}$$

where

$$\mathbf{j}=(\hbar/2mi)(\psi_{\mathbf{k}'}^*\,\mathrm{grad}\psi_{\mathbf{k}}-\psi_{\mathbf{k}}\,\mathrm{grad}\psi_{\mathbf{k}'}^*). \tag{19}$$

Then, having in mind that the vector $\mathbf{j}\exp(i\mathbf{q}\cdot\mathbf{r})$ has the exact periodicity of the lattice, one may obtain the following:

$$I_0=\frac{\hbar\mathbf{q}}{E(\mathbf{k}')-E(\mathbf{k})}\cdot\int\mathbf{j}\exp(i\mathbf{q}\cdot\mathbf{r})d\mathbf{r}. \tag{20}$$

For small q, this reduces to

$$I_0 = (\hbar^2/N\epsilon mi)\mathbf{q}\cdot\mathbf{A}(\mathbf{H},\mathbf{k}), \tag{21}$$

where $\mathbf{A}(\mathbf{H},\mathbf{k})$ is the coefficient of $\exp(2\pi i\mathbf{H}\cdot\mathbf{r})$ in the Fourier expansion of the function $u_{\mathbf{k}+2\pi\mathbf{H}}{}^{*}\,\mathrm{grad}u_{\mathbf{k}}$, and ϵ is the excitation energy as given in Eq. (10).

Using Eqs. (1), (13), and (21), one obtains the following:

$$Pd\Omega' = (2\hbar^2e^4/mE_p\epsilon^2)\,|\mathbf{q}\cdot\mathbf{A}|^2q^{-3}dqd\phi. \tag{22}$$

This expression refers to the probability of excitation of a single metal electron from $\mathbf{k}$ to $\mathbf{k}+2\pi\mathbf{H}$. For the required summation over initial states, one may introduce the volume element

$$d\mathbf{k} = dSd\epsilon/|\mathrm{grad}_{\mathbf{k}}\epsilon|, \tag{23}$$

where dS is an element of area in a surface of constant ϵ. On introducing the density of states in $\mathbf{k}$-space, one then has the following contribution to $Q(\epsilon)$:

$$\left(\frac{\hbar^2e^4}{2\pi^3mE_p\epsilon^2}\right)\frac{|\mathbf{q}\cdot\mathbf{A}|^2dSdqd\phi}{|\mathrm{grad}_{\mathbf{k}}\epsilon|\,q^3}. \tag{24}$$

We next consider the summation over $\mathbf{H}$, confining attention to cubic metals, since results for these are essentially simpler than for metals of lower symmetry. Moreover, we will make explicit statements for the body-centered cubic case, which is of immediate interest, and only indicate the minor changes which are required to cover the face-centered case. The first set of reciprocal lattice vectors corresponding to nonvanishing values of $\mathbf{A}$ are given by $\mathbf{H}=\mathbf{n}/a$, where a is the lattice constant, and $\mathbf{n}$ is one of the twelve vectors with integer components for which $n^2=2$. One way of carrying out the summation over these vectors is suggested by Butcher's treatment of the corresponding point in his work on photoelectric absorption.[13] It becomes apparent that $\sum_{\mathbf{n}}$ is equivalent to $\frac{1}{4}\sum_R$, where R represents one of the 48 operations of the cubic group. Also, for any pair of vectors, such as $\mathbf{q}$ and $\mathbf{A}$,

$$\sum_R|\mathbf{q}\cdot R\mathbf{A}|^2 = 16q^2|\mathbf{A}|^2. \tag{25}$$

Summing Eq. (24) over $\mathbf{H}$ with these results in mind, one finds

$$\left(\frac{2\hbar^2e^4}{\pi^3mE_p\epsilon^2}\right)\frac{|\mathbf{A}|^2dSdqd\phi}{|\mathrm{grad}_{\mathbf{k}}\epsilon|\,q}. \tag{26}$$

Integration then yields

$$Q(\epsilon) = \frac{2\hbar^2e^4}{\pi^2mE_p\epsilon^2}\ln\left(\frac{2E_p}{\epsilon}\right)\int\frac{|\mathbf{A}|^2dS}{|\mathrm{grad}_{\mathbf{k}}\epsilon|}. \tag{27}$$

One notices that there is no dependence of $Q(\epsilon)$ upon the orientation of the crystal with respect to the primary beam. This point appears to have been missed in previous treatments of the scattering problem, but the corresponding point for optical excitation was emphasized by Butcher.

5. RELATIONSHIP TO PHOTOELECTRIC ABSORPTION

Equation (20) of Butcher's paper gives his result for the photoelectric contribution to the absorbing power[14] of a cubic metal. When written in our notation, and restricted to transitions to the second Brillouin zone of a body-centered cubic metal, this equation becomes

$$\sigma_p(\omega) = \frac{e^2\hbar^2}{\pi^2m^2\omega}\int\frac{|\mathbf{A}|^2dS}{|\mathrm{grad}_{\mathbf{k}}\epsilon|}. \tag{28}$$

On combining Eqs. (27) and (28), one obtains

$$Q(\epsilon) = (2e^2m/\hbar E_p\epsilon)\,\ln(2E_p/\epsilon)\sigma_p(\omega), \tag{29}$$

where $\omega=\epsilon/\hbar$. This equation applies to all cubic metals. For the face-centered case the first set of reciprocal lattice vectors are the eight for which $n^2=3$. To be applicable to these transitions, Eqs. (27) and (28) would have to be modified by the introduction of an additional factor $\frac{2}{3}$ on the right, while Eq. (29) would remain unchanged.

6. APPLICATION TO SEVERAL ALKALI METALS

For sodium, potassium, and rubidium, Butcher has shown that the optical data of Ives and Briggs for the visible and near ultraviolet spectrum may be adequately interpreted by ascribing most of the absorption to photoelectric excitation of conduction electrons which are nearly free.[15] Butcher's expression for the photoelectric absorbing power, given in Eq. (26) of reference 7, is

$$\sigma_p(\omega) = (\sqrt{2}mae^2/4\pi^2\hbar^4)\,|V_{\surd 2}|^2(\omega-\omega_0)(\omega_1-\omega)\omega^{-3}. \tag{30}$$

Inserting this into our Eq. (29) yields

$$Q(\epsilon) = (m^2ae^4/\sqrt{2}\pi^2\hbar^4E_p)\,|V_{\surd 2}|^2 \times\ln(2E_p/\epsilon)(\epsilon-\epsilon_0)(\epsilon_1-\epsilon)\epsilon^{-4}. \tag{31}$$

In these equations, $|V_{\surd 2}|$ is the Fourier coefficient of the lattice potential for $n=\sqrt{2}$, while $\epsilon_0=\hbar\omega_0$ and $\epsilon_1=\hbar\omega_1$, are minimum and maximum values of the excitation energy. When the free-electron equation for energy is used, these limiting energies are given by $(4\pi^2\hbar^2/ma^2)(1\mp\gamma)$, where $\gamma=k_0a/\pi\sqrt{2}$, k_0 being the radius of the Fermi sphere. For an electron density $2/a^3$ (that is, one electron per atom) $k_0a=(6\pi^2)^{\frac{1}{3}}$, and $\gamma=0.8773$. This corresponds to $\epsilon_0=0.64E_0$ and $\epsilon_1=9.76E_0$, where $E_0=\hbar^2k_0{}^2/2m$ is the maximum Fermi energy.

In accounting for the observed optical data for each

---

[13] See especially Eqs. (2), (3), and (5), and Sec. 4 of reference 7.

[14] The absorbing power is so defined that multiplication by the mean square electric field gives the mean rate of absorption of electromagnetic energy per unit volume.

[15] For cesium, the nearly free electron model was not satisfactory. This has no bearing on the applicability of Eq. (29), but does mean that cesium is a less convenient metal to use in illustrating the theory than are the metals considered.

of the three alkalis, Butcher had only the parameter $|V_{\sqrt{2}}|$ at his disposal. The required values proved to be 0.323 ev (Na), 0.305 ev (K), and 0.350 ev (Rb), which are quite reasonable. In the case of sodium, Howarth and Jones[16] have remarked that their theoretical value for the energy gap at the center of a face of the Brillouin zone (0.65 ev) is just twice Butcher's value of $|V_{\sqrt{2}}|$, as it should be in the approximation of nearly free electrons.

In view of Butcher's success with Eq. (30) for $\sigma_p(\omega)$, it is reasonable to give serious attention to the implications of the corresponding expression for $Q(\epsilon)$. Turning to Eq. (31), one notices that the logarithmic factor varies relatively slowly with ϵ, while the product of the remaining factors varies rapidly and has a maximum at $\epsilon=1.3\epsilon_0$. Accordingly, no significant error is made if ϵ is replaced by ϵ_0 in the logarithm. For the total number of umklapp processes per unit primary path which leave the excited electron in the second Brillouin zone, one then obtains

$$\frac{dN_e}{dX}=\int_{\epsilon_0}^{\epsilon_1} Q(\epsilon)d\epsilon=\left(\frac{\sqrt{2}m^3a^3e^4}{6\pi^4\hbar^6E_p}\right)\frac{\gamma^3|V_{\sqrt{2}}|^2}{(1-\gamma^2)^2}\ln\left(\frac{2E_p}{\epsilon_0}\right). \tag{32}$$

When numerical values are inserted and the logarithm converted to the base 10, Eq. (32) becomes

$$dN_e/dX=0.033a^3|V_{\sqrt{2}}|^2E_p^{-1}\log(2E_p/\epsilon_0), \tag{33}$$

where energies are in electron volts and lengths in angstroms. Taking rubidium, with $a=5.62$ A and $|V_{\sqrt{2}}|=0.350$ ev, as an example, one obtains

$$dN_e/dX=(0.72/E_p)\log(1.7E_p). \tag{34}$$

For $E_p=500$ ev, this gives an excitation rate of 4.2 per 1000 A. For sodium and potassium, the excitation rates are somewhat smaller, being 1.5 and 2.7 per 1000 A, respectively, at the same primary energy.

The distribution in energy of the transitions is determined by the function

$$(\epsilon-\epsilon_0)(\epsilon_1-\epsilon)\epsilon^{-4}. \tag{35}$$

The rise from the threshold at ϵ_0 is rapid, the maximum of the distribution being reached at $1.3\epsilon_0$, and 80% of all transitions falling below $\epsilon=3\epsilon_0$. The average excitation energy turns out to be $2.35\epsilon_0$, which is substantially smaller than some of the rough estimates which have been made in the past. For rubidium, $\epsilon_0=1.17$ ev, and the corresponding rate of energy loss for a 500-ev primary is only 12 ev per 1000 A. In order of magnitude, this is probably 10% of the contribution of the conduction electrons to the energy loss, and one percent of the total energy loss.

7. IMPORTANCE OF VARIOUS TYPES OF EXCITATION FOR SECONDARY EMISSION

The results presented above indicate that for the alkalis the umklapp processes are of no importance for primary energy loss, and suggest that they are of minor importance for secondary electron emission. For example, in rubidium a 500-ev primary might have a range of about 100 A, and cause two or three umklapp processes. Keeping in mind that only a fraction of the excited electrons start out in a favorable direction and with sufficient energy for emission, and that they are likely to lose most of their energy in a distance substantially smaller than the primary range, it would appear optimistic to expect an emission of the order of 0.1 secondary per primary from this source. On the other hand, the measured emission coefficient for rubidium at the assumed primary energy has been reported to be about 0.9.

In spite of the above remarks, one would not be justified in neglecting the umklapp processes in treating secondary emission from the alkalis unless other processes had been shown to be much more productive. Thus, further information concerning transitions with $\mathbf{H}=0$ is important. In order to reach rough estimates one may ignore the periodic field in the metal and treat the conduction electrons as though they were completely free. In view of the remarks following Eq. (6) one may then place $I=1$ in Eq. (1), obtaining

$$Pd\Omega'=(4m^2e^4K'/\hbar^4q^4K)d\Omega'. \tag{36}$$

To arrive at a suitable approximation for $d\Omega'$, consider the following equation, which may easily be verified

$$K^2K'^2-(\mathbf{K}\cdot\mathbf{K}')^2=q^2K'^2-(\mathbf{q}\cdot\mathbf{K}')^2. \tag{37}$$

Now, because of the momentum and energy laws, $\mathbf{q}\cdot\mathbf{K}'=\mathbf{q}\cdot\mathbf{k}$. Hence, if the angle between $\mathbf{K}'$ and $\mathbf{K}$ is again denoted by θ, Eq. (37) implies

$$K^2\sin^2\theta=q^2-(\mathbf{q}\cdot\mathbf{k}/K')^2. \tag{38}$$

This is an exact relationship which is simplified when the primary energy is much larger than the energy of the metal electrons and the excitation energy. One may then neglect the last term on the right, and obtain the approximation $K\theta=q$ which corresponds to

$$d\Omega'=2\pi qdq/K^2. \tag{39}$$

Inserting Eq. (39) into Eq. (36), and also introducing the primary energy, one has

$$Pd\Omega'=(4\pi me^4/\hbar^2E_p)q^{-3}dq. \tag{40}$$

This equation gives the differential cross section for scattering involving a momentum transfer in the range $\hbar dq$ near $\hbar q$, and can, of course, be obtained by classical methods. In fact, the classical approach to the problem formed the basis of the author's 1950 paper on secondary emission,[17] and Eq. (4) of that paper differs from Eq. (40) above only in notation.

---

[16] D. J. Howarth and H. Jones, Proc. Phys. Soc. (London) **A65**, 355 (1952).

[17] E. M. Baroody, Phys. Rev. **78**, 780 (1950). More recent studies of secondary emission theory which treat the conduction electrons as free have been made by P. A. Wolff [Phys. Rev. **95**, 56 (1954)] and W. Brauer [O. Hachenberg and W. Brauer, Fortschr. Physik **1**, 439 (1954)]. However, these authors deal mainly with such

It is important to recognize that the approximations leading to Eq. (40) depend only on K being large compared to k and k'. The assumption $k \ll k'$ was not introduced here, or in the 1950 paper. One may then ask why our result differs from that of Dekker and van der Ziel[18] except in the limiting case $k=0$. In our judgment, the disagreement arises because Dekker and van der Ziel use an expression for $d\Omega'$ which is correct only for $k \ll k'$. To make this clear, one may introduce $q^2=k'^2-2\mathbf{k}\cdot\mathbf{q}-k^2$ into Eq. (38), obtaining

$$K^2 \sin^2\theta = k'^2-2\mathbf{k}\cdot\mathbf{q}-k^2-(\mathbf{q}\cdot\mathbf{k}/K')^2. \tag{41}$$

For a fast primary and $k \ll k'$, Eq. (41) reduces to $K\theta = k'$ which yields

$$d\Omega' = 2\pi k' dk'/K^2. \tag{42}$$

This is the result of Dekker and van der Ziel, and it is evidently less general than Eq. (39).

In reference 17, the production of secondaries per unit primary path with final energy exceeding $\mu^2 E_0$ was found to be

$$3.0E_0^{\frac{1}{2}}/E_p(\mu^2-1), \tag{43}$$

energies being in electron volts and distances in angstroms. On the other hand, if energies are estimated using the free-electron formula, the lowest state in the second Brillouin zone of the body-centered cubic metals falls at $1.30E_0$. Thus, a rough estimate of the number of collisions with $\mathbf{H}=0$ per unit primary path in which the metal electron receives at least enough energy to reach the second Brillouin zone is $10E_0^{\frac{1}{2}}/E_p$. For $E_p=500$ ev, this gives 35, 28, and 27 excitations per 1000 A for sodium, potassium, and rubidium, respectively. These numbers are substantially larger than the corresponding results for $\mathbf{H}\neq 0$, but the difference is not great enough to justify neglecting the umklapp processes. Another important point must also be mentioned. The estimates of the total production of secondaries by collisions of both types are somewhat lower than would appear to be required by experimental emission coefficients. Since this statement is not the result of a complete analysis of the emission process, it should not be taken too seriously. However, it is a reminder that there may be important contributions from innershell electrons. In rubidium, for example, the ionization potential for the six $4p$ electrons of the free atom is 20 volts. Thus, the corresponding energy band in the solid is not so far below the conduction band and may make a significant contribution to secondary emission caused by a 500-ev primary.

In an effort to reach some conclusions concerning the inner electrons, one may use the approximate cross section for ionization of a free atom by loss of an electron from the shell nl, which was originally derived by Bethe[19]:

$$\Phi_{nl}=\frac{\pi e^4 c_{nl} Z_{nl}}{|E_{nl}|E_p}\ln\left(\frac{4E_p}{C_{nl}}\right). \tag{44}$$

In this equation, Z_{nl} is the number of electrons in the shell, $|E_{nl}|$ is its ionization potential, and $C_{nl}\sim|E_{nl}|$. The coefficients c_{nl} were listed by Bethe and range from 0.05 to 0.3. To apply Eq. (44) here, one may multiply by the density of atoms in the solid, take $C_{nl}=|E_{nl}|$, and sum over all shells for which $|E_{nl}|<E_p=500$ ev. In this way, one obtains 3.3, 5.0, and 3.6 ionization per 1000 A in sodium, potassium, and rubidium respectively. These numbers, being rough indications at best, and having turned out neither very large nor very small, do not permit a conclusion concerning the importance of the inner shells. However, they suggest that the inner electrons are important and should be considered in theories of secondary emission.

ACKNOWLEDGMENTS

The author has had frequent opportunities to discuss this work with Dr. R. J. Harrison, and wishes to thank him for many valuable comments. He would also like to thank Dr. T. J. Krieger for making a careful review of the manuscript.

---

processes as the diffusion, slowing down, and multiplication of the internal secondaries, rather than with the questions which are of principal concern in the present paper.

[18] See page 758 of reference 10. Their definition of θ is not the same as that used here and appears to be the source of the difference discussed in the foregoing.

[19] See N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, London, 1949), second edition, p. 247, Eq. (50).