constant in primary energy suggests diffraction followed by inelastic background scattering as in the first case considered. However, in the present case the maxima occur at about 118 ev which is 3.5 ev greater than the 114.5 ev for the diffraction peak. As in the first case we may associate this difference with a variation in the effective value of inner potential. It may also be attributed to a discrete energy loss of 3.5 ev (which agrees approximately with the value for the first discrete loss peak) which precedes the diffraction. The experimental evidence is not sufficient to justify a definite conclusion. The number of observations was limited by a failure in the experimental tube.

SUMMARY

The following processes have been postulated to interpret the results:

(1) For the results in the vicinity of the 59.5-ev diffraction beam.—Diffraction followed by inelastic background scattering. However, the maxima occur at 3.5 ev below the 59.5 ev of the diffraction beam.

(2) For the results in the vicinity of the 114.5-ev diffraction beam.—(a) Inelastic background scattering followed by diffraction, for energy losses below 10 ev. The maxima occur at the secondary energy of 114.5 ev which checks with the 114.5-ev diffraction peak. (b) The same as (a) plus diffraction followed by inelastic background scattering, for energy losses above 10 ev. The maxima for the latter process occur at 118 ev instead of at 114.5 ev which corresponds to the diffraction maximum.

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The Surface Photoelectric Effect

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An expression is derived for the photoelectric current produced at the surface of a metal, the conduction electrons being supposed free and the potential barrier of arbitrary shape. The validity of the common assumption that the current arising from conduction electrons of a particular momentum can be expressed as the product of an excitation function and a transmission coefficient is examined. It is concluded that the assumption is in general valid. The production in the photoelectric current of beat frequencies between spectral lines is also briefly discussed.

I. INTRODUCTION

In discussions of the surface photoelectric effect in metals, particularly in deriving an expression for the threshold frequency at 0°K from data obtained at higher temperatures, it has frequently been assumed that the photoelectric current arising from conduction electrons of given momentum in the metal may be expressed as a product of an excitation function and the transmission coefficient of the surface barrier for the excited electrons. The excitation function is then assumed not to vary rapidly near the threshold frequency.

No general proof of the validity of this factorization appears to have been given in accessible literature, but doubts as to its validity have been expressed.[1,2]

An extension of earlier work[3] is given below in which a formal expression of great generality for the photoelectric current is derived. From this it appears that the factorization mentioned and the smooth variation of the excitation function near the threshold are in general justified. The theory is easily extended to enable discussion of the possible production of beats between spectral lines.

II. ASSUMPTIONS

If we suppose that the conduction electrons are free in the interior of the metal and neglect their interaction, the potential energy of each may be represented near the surface by a potential $V(x)$ which has some such form as shown in Fig. 1(a).

The wave function u for an electron unperturbed by incident light satisfies

$$(\hbar^2/2m)\nabla^2 u + i\hbar\partial u/\partial t - Vu = 0. \tag{1}$$

Putting

$$u = u_k = \psi_k \exp(-iE_k t/\hbar), \tag{2}$$

let

$$\psi_\kappa = \alpha_k \phi_k(x) \exp(ik_2 y + ik_3 z);$$

then

$$\phi_\kappa'' - \{p^2 + (\mu/h)V(x)\}\phi_k = 0,$$

where

$$p = (\mu\nu_a - k_1^2)^{\frac{1}{2}} > 0, \quad \mu = 8\pi^2 m/h,$$

$$k^2 = k_1^2 + k_2^2 + k_3^2 = (8\pi^2 m/h^2)(E_k + h\nu_a).$$

[1] R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, London, 1936), p. 358.

[2] E. Guth and C. J. Mullin, Phys. Rev. **59**, 868 (1941).

[3] R. E. B. Makinson, Proc. Roy. Soc. **A910**, 367 (1937). The same notation is used here. Essentially the present discussion was given in a Dissertation by the author, University of Cambridge, England, 1938.

In the interior of the metal

$$\phi_k = \exp(ik_1x) + a_k \exp(-ik_1x)$$

with $|a_k| = 1$. We restrict k_1 to positive values.

At temperature $T = 0°\text{K}$, $k \leqslant k_0$ where k_0 gives the electron wave number at the top of the Fermi distribution, so that $k_0^3/3\pi^2 = n_0$, the number of conduction electrons per cm^3. The normalizing factor α_k is supposed chosen so in the interior of the metal

$$2\textstyle\sum_k |\psi_k|^2 = n_0,$$

i.e.,

$$\alpha_k^2 = (1/8\pi^3)dk_1dk_2dk_3 \text{ at } T = 0°\text{K}.$$

For generality in the following discussion we note that Bardeen[4] has shown that a more accurate description of the electron gas than is given above may be obtained by replacing the potential $V(x)$ in (1) by the effective potential

$$U_k(x) = V(x) - B_k(x),$$

in which

$$B_k(x) = (1+c)A_k(x),$$

the function $A_k(x)$ representing an exchange energy and $cA_k(x)$ a "correlation energy," both being dependent on $\boldsymbol{k}$. "Each electron has, so to speak, to have its own barrier." The constant c was assigned the value 0.24 by Bardeen and calculations of $B_k(x)$ were given for sodium. We suppose therefore in the following that u satisfies the unperturbed wave equation,

$$(h^2/8\pi^2m)\nabla^2u - (h/2\pi i)\partial u/\partial t - U_k(x)u = 0, \quad \text{(1a)}$$

where the functions $U_k(x)$ are of the general form* sketched in Fig. 1(b).

We will further assume that all the barriers tend towards the form of an image-field barrier[5] of shape $-e^2/4x$ as $x \to \infty$, $B_k(x)$ vanishing faster than the latter function.

III. THE PHOTOELECTRIC CURRENT

In the presence of incident plane waves of light of frequency ν, which we may describe classically by a vector potential $\boldsymbol{A}$ and scalar potential Φ, a perturbation is introduced into (1a); thus, neglecting a term in A^2,

$$(h^2/8\pi^2m)\nabla^2u - (h/2\pi i)\partial u/\partial t - U_k(x)u \\ = -(ihe/2\pi mc)(\boldsymbol{A}\cdot\nabla u + \tfrac{1}{2}u\nabla\cdot\boldsymbol{A}) - e\Phi u. \quad (3)$$

We may put $\Phi = 0$ and

$$\boldsymbol{A}(x, y, t) = \boldsymbol{a}(x) \exp\{-2\pi i\nu(y \sin\theta/c + t)\} \\ + \text{conjugate},$$

where θ is the angle of incidence of the light and y a cartesian coordinate in the plane of the surface and the plane of incidence.

Let $u = u_k + v_k$ where u_k is the solution corresponding to (2) of the unperturbed Eq. (1a). Then to the first order

$$(h^2/8\pi^2m)\nabla^2v_k - (h/2\pi i)\partial v_k/\partial t - U_k(x)v_k \\ = -(ihe/2\pi mc)(\boldsymbol{A}\cdot\nabla u_k + \tfrac{1}{2}u_k\nabla\cdot\boldsymbol{A}).$$

Neglecting the terms in $\exp\{-2\pi i(E_k - h\nu)t/h\}$, which correspond to stimulated emission, and putting

$$v_k = \alpha_k\vartheta_k(x) \exp\{ik_2y + ik_3z - 2\pi i(E_k + h\nu)t/h \\ - 2\pi i\nu y \sin\theta/c\},$$

we find that ϑ_k must satisfy

$$\vartheta_k'' + \{r^2 - (\mu/h)U_k(x)\}\vartheta_k = -(4\pi ie/ch) \\ \times\{a_x\phi_k' + i\phi_k(a_yk_2 + a_zk_3) + \tfrac{1}{2}\phi_k ka_x'\}, \quad (4)$$

on neglecting two small terms involving ν/c, where

$$r = \{k_1^2 + \mu(\nu - \nu_a)\}^{\frac{1}{2}} > 0,$$

and ν_a is now the function of $\boldsymbol{k}$ given by

$$h\nu_a = -U_k(-\infty).$$

We have to find the solution of (4) which for large positive x represents an outward stream of photoelectrons:

$$\vartheta_k = B_re^{irx}, \quad x \gg 0, \\ = C_re^{-iqx}, \quad x \ll 0,$$

where

$$q = (k_1^2 + \mu\nu)^{\frac{1}{2}}.$$

Let $\chi_r(x)$ be the solution of

$$\chi_r'' + \{r^2 - (\mu/h)U_k(x)\}\chi_r = 0, \quad (5)$$

which satisfies the boundary conditions

$$\chi_r = e^{-iqx}, \quad x \ll 0 \\ = G_re^{irx} + H_re^{-irx}, \quad x \gg 0. \quad \text{(5a)}$$

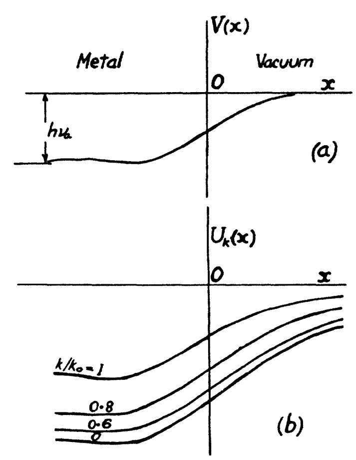

FIG. 1. (a) General shape of potential barrier at metal surface, supposed independent of electron momentum $\boldsymbol{k}h$. (b) Barrier dependent on k (see reference 4).

[4] J. Bardeen, Phys. Rev. **49**, 653 (1936).
* See reference 4, p. 661.
[5] J. Bardeen, Phys. Rev. **49**, 640A (1936); **58**, 727 (1940).

Multiplying both sides of (4) by χ_r, integrating from $-\infty$ to $+\infty$ with an extinction factor $e^{\Delta x}$ (Δ small), using (5) and integrating by parts, we find

$$B_r = (2\pi e/hc) M(\mathbf{k}, \nu)/(H_r r),$$

where

$$M(\mathbf{k}, \nu) = \int_{-\infty}^{\infty} \{a_x \chi_r \phi_k' + \tfrac{1}{2}\phi_k \chi_r a_x' + i\chi_r \phi_k (k_2 a_y + k_3 a_z)\} dx. \quad (6)$$

Now the photoelectric current density in $x \gg 0$ corresponding to ϑ_k is

$$dJ_x = (2eh/4\pi mi)(v_k \partial v_k^*/\partial x - v_k^* \partial v_k/\partial x) = -(eh/\pi m)|\alpha_k|^2 r |B_r|^2. \quad (7)$$

The transmission coefficient of the barrier $U_k(x)$ to the wave e^{-irx} incident from the outside (or e^{iqx} incident from inside) is

$$D(r) = q/(r|H_r|^2),$$

hence

$$dJ_x = -|\alpha_k|^2 e \cdot D(r) \cdot (4\pi e^2/hmc^2 q) |M(\mathbf{k}, \nu)|^2. \quad (7a)$$

It is to be noted that this contribution to the photoelectric current, arising from the electrons with momentum $\mathbf{k}h$, is in the form of the product of the electronic charge, the normalizing factor $|\alpha_k|^2$, $D(r)$ the transmission coefficient of the barrier for the excited electrons, and the function $4E(\mathbf{k}, \nu)$ where

$$E(\mathbf{k}, \nu) = (\pi e^2/hmc^2 q)|M(\mathbf{k}, \nu)|^2. \quad (8)$$

We may describe $E(\mathbf{k}, \nu)$ as the probability per unit time of the excitation of one electron per cm^2 of surface from an unperturbed state $\mathbf{k}$ to that of an outgoing photoelectron. (There are four electrons in the state $\mathbf{k}$ with the normalization used here.)

Integrating over all values of $\mathbf{k}$, we have for the photoelectric current density in e.s.u. per cm^2 at 0°K:

$$J_x = (-e/2\pi^3) \int\int\int E(\mathbf{k}, \nu) D(r) dk_1 dk_2 dk_3, \quad (9)$$

the integration being taken over the hemisphere in $\mathbf{k}$ space: $k_1^2 + k_2^2 + k_3^2 \leqslant k_0^2$, $k_1 > 0$.

In principle, the value of the vector potential $\mathbf{A}$ near the surface may be calculated[3] from classical wave theory and a knowledge of the electron density variation near the surface, the latter being calculable from the unperturbed wave functions u_k.

If the surface is "perfectly plane" (i.e., with irregularities small not merely in comparison with a light wave-length but with the electron wave-lengths as at a face of a perfect crystal) it may be shown[3] that a_y and a_z are nearly constant through the region in which $U_k(x)$ varies appreciably, which is much less than a light wave-length. The component a_x, on the other hand, varies rapidly in this region, inversely as the dielectric constant $\epsilon_1(x) + i\epsilon_2$ where $\epsilon_1(x) = 1 - ne^2/(\pi m \nu^2)$ and ϵ_2 has a small value representing damping. In this case the photoelectric current arises only from the component of the incident light polarized in the plane of incidence and vanishes for normal incidence. If, now, following Bardeen,[4] the function $U_k(x)$ is supposed to depend only on the magnitude of k and not upon its direction, the excitation function $E(k, \nu)$ simplifies to the form

$$E(k, k_1, \nu) = (e^2/64\pi hm) H_z(0)^2 \times \sin^2\theta |N(k, k_1, \nu)|^2/(\nu^2 q), \quad (10)$$

where $H_z(0)$ is the amplitude of the z-component of the magnetic field at the surface and

$$N(k, k_1, \nu) = \int_{-\infty}^{\infty} (\chi_r \phi_k' - \phi_k \chi_r')/\{\epsilon_1(x) + i\epsilon_2\} dx.$$

The results obtained previously[3] for a square barrier, representing potassium, are easily seen to follow from the foregoing as a special case.

The effect of optical roughness of the surface, the scale of irregularities being greater than a light wave-length, results in emission for any polarization or angle of incidence,[6] but for monochromatic light one can show that it remains of the form

$$J = \text{const.} G(\nu) \cdot R$$

where

$$G(\nu) = (1/\nu^2) \int\int\int [D(r)/q] \times |N(k, k_1, \nu)|^2 dk_1 dk_2 dk_3 \quad (11)$$

and R is a purely geometrical factor describing the roughness of the surface, involving also the angle of incidence and plane of polarization.

The same conclusion holds** when there exists roughness on a scale small compared with a light wave-length but large when compared with the barrier width or when both types of roughness are present together.

IV. THE EXCITATION FUNCTION

We conclude that it is legitimate in all cases to regard the photoelectric current, arising as a surface effect from electrons of a given momentum

[6] K. Mitchell, Proc. Roy. Soc. **A153**, 513 (1936).

** See reference 3. The more general barrier here considered does not affect the essentials of the discussion.

$\boldsymbol{k}h$ within the metal, as the product of an excitation function and a barrier transmission coefficient.

This formal separation is of course of little value unless the excitation function $E(\boldsymbol{k}, \nu)$ given by (8) does not in fact vary sharply with frequency in the neighborhood of the threshold frequency ν_g. We need therefore to show that the function $M(\boldsymbol{k}, \nu)$ given by (6) cannot vary sharply near ν_g.

In the integrand of (6) we see from (5a) that $\chi_r(x)$ is not critically dependent on ν near ν_g (i.e., as $r\rightarrow 0$) except for values of x near the top of the surface barrier, but in that region the factor $\phi_k(x)$ is falling off exponentially and has become small; we are also well away from the maximum of a_x. Further, if the barrier is always of the image type for large x, as appears to be the case, the transmission coefficient $D(r)$ for the wave χ_r (an incoming wave with the transmitted portion always of unit amplitude) approaches a limit[7] only a little less than 1 as $r\rightarrow 0$. Thus G_r and H_r increase no faster than r^{-1} as $r\rightarrow 0$.

It seems clear then, that in general, the major contribution to the integral (6) arises from vaues of x where the integrand does not vary sharply with ν near ν_g although lengthy numerical calculations would be necessary to make a quantitative statement in a particular case. We therefore expect the integral (6) and hence the excitation function to vary smoothly with frequency near the threshold.

It has sometimes been assumed[8, 9] that the excitation function is proportional to the component of electron momentum normal to the surface. Equations (8) and (10) give no support to this assumption.

It may be added that the theory of the temperature-dependence of the photoelectric current near the threshold is complicated in a different manner by the dependence, referred to above, of the effective surface barrier on the momentum of the conduction electron excited. This invalidates the expressions given by Fowler[1] and by Du Bridge, to an extent uncertain in the absence of numerical computation for particular cases. Conclusions based on discrepancies found experimentally,[10–12] for which other reasons have been advanced[13] are therefore in some doubt. Similar remarks apply to expressions which have been derived for the total energy distribution of photoelectrons.[6, 8]

[7] L. W. Nordheim, Proc. Roy. Soc. **A121**, 626 (1928).
[8] A. G. Hill, Phys. Rev. **53**, 184 (1938).
[9] H. Bradner, Phys. Rev. **71**, 269 (1947).
[10] M. M. Mann and L. A. Du Bridge, Phys. Rev. **51**, 120 (1937).
[11] R. J. Cashman, Phys. Rev. **52**, 512 (1937).
[12] C. F. J. Overhage, Phys. Rev. **52**, 1039 (1937).
[13] W. V. Houston, Phys. Rev. **52**, 1047 (1937).

V. BEATS BETWEEN SPECTRAL LINES

It has been proposed[14] to excite a resonant cavity at microwave frequencies by means of "beats" in the photoelectric current produced by two sharp adjacent spectral lines. The general expressions given above enable the possibility of this to be examined from another angle.

If we assume for simplicity that both spectral lines are perfectly sharp, with frequencies ν_1 and ν_2 we start as before from (3), putting $\Phi=0$, and

$$A(x, y, z, t)=\boldsymbol{a}_1(x)\exp\{-2\pi i\nu_1(y\sin\theta_1/c+t)\}+\boldsymbol{a}_2(x)\exp\{-2\pi i\nu_2(y\sin\theta_2/c+t)\}+\text{conjugates}.$$

We now put

$$v_k=\alpha_k\vartheta_k^{(1)}(x)\exp\{ik_2y+ik_3z-2\pi i(E_k+h\nu_1)t/h-2\pi i\nu_1y\sin\theta_1/c\}+\alpha_k\vartheta_k^{(2)}(x)\times\exp\{ik_2y+ik_3z-2\pi i(E_k+h\nu_2)t/h-2\pi i\nu_2y\sin\theta_2/c\}$$

and find that $\vartheta_k^{(1)}$ and $\vartheta_k^{(2)}$ both satisfy equations of the form (4) with ν_1, ν_2 written respectively for ν. We write r_1, r_2 for r and $B_r^{(1)}$, $B_r^{(2)}$ for B_r when $\nu=\nu_1$, ν_2. Let $B_r^{(1)}=|B_r^{(1)}|\exp(i\delta_1)$, $B_r^{(2)}=|B_r^{(2)}|\times\exp(i\delta_2)$. Equation (7) for the photoelectric current arising from electrons with a particular value of $\boldsymbol{k}$ now becomes

$$dJ_x=-(eh/\pi m)|\alpha_k|^2\{r_1|B_r^{(1)}|^2+r_2|B_r^{(2)}|^2+(r_1+r_2)|B_r^{(1)}B_r^{(2)}|\cos[(r_1-r_2)x-2\pi(\nu_1-\nu_2)t+(\delta_1-\delta_2)]\}. \quad (12)$$

It is clear from (12) that, at fixed x, the current varies at the "beat" frequency. If $\nu_1-\nu_2$ is very small, so that $\nu_1\sim\nu_2\sim\nu$ say and $B_r^{(1)}\sim B_r^{(2)}$, the current oscillates sinusoidally between zero and twice its mean value, i.e., with 100 percent modulation.

However, the expression (12) has to be integrated over all values of $\boldsymbol{k}$ for which $r_{1,2}>0$. The total electron stream thus contains components with a continuous range of velocities from zero up to that of the most energetic photo-electrons ejected at frequency ν; each component is intensity-modulated, the phase $(\delta_1-\delta_2)$ of the modulation at $x=0$ varying with velocity. The percentage modulation of the total photoelectric current at the beat frequency is therefore certainly very small.

ACKNOWLEDGMENT

The writer is greatly indebted to Mr. A. H. Wilson for helpful discussions during the period when much of the above work was done.

[14] A. T. Forrester, W. E. Parkins, and E. Gerjuoy, Phys. Rev. **72**, 728 (1947); also **73**, 922 (1948).