tron in a pure magnetic field are well known,[3] and admit of a continuum of energy levels

$$E=(e\hbar H/2mc)(2\nu+m_l+|m_l|+1)+E_z, \quad \nu=0,1,2,\cdots, E_z\geqq 0, \tag{11}$$

because of the free motion along the field (z direction). We now apply the adiabatic approximation, using the Coulomb field to restrict the motion in the z direction. This gives us a potential for the z motion that is an average of the Coulomb field over the x, y plane for each value of z. We are interested only in the lowest state $\nu=0$, and in $m_l=0, \pm 1$; the z potential is then:

$$\begin{aligned} U_0(z)&=-2e^2\beta^{\frac{1}{2}}\exp(\beta z^2)Erfc(|z|\beta^{\frac{1}{2}}), \quad m_l=0,\\ U_1(z)&=-e^2[\beta|z|+\beta^{\frac{1}{2}}\exp(\beta z^2)(1-2\beta z^2)\\ &\quad\times Erfc(|z|\beta^{\frac{1}{2}})], \quad m_l=\pm 1,\\ U_0(0)&=2U_1(0)=-e^2(\pi\beta)^{\frac{1}{2}},\\ &U_0\rightarrow U_1\rightarrow -e^2/|z|, \quad \text{as} \quad |z|\rightarrow\infty;\\ &Erfc(x)\equiv\int_x^\infty e^{-t^2}dt;\\ &\beta\equiv eH/2\hbar c. \end{aligned} \tag{12}$$

[3] Cf. Condon and Morse, *Quantum Mechanics* (McGraw-Hill, 1929), p. 79.

Thus U_0 had twice the depth of U_1 at $z=0$ and the same asymptotic form; it can also be shown quite readily that U_0 is less than U_1 for all finite values of z. The total energy is then given approximately by (11), where E_z is now an eigenvalue of the equation:

$$\frac{d^2\chi}{dz^2}+\frac{2m}{\hbar^2}[E_z-U(z)]\chi=0.$$

Then for energies just below the series limit, the eigenvalues for the case $m_l=0$ will be more closely spaced than those for the case $m_l=\pm 1$, since the potential U_0 is considerably deeper than the potential U_1. While this conclusion cannot apply even qualitatively as far from the series limit as the beginning of region III, it serves as another indication that the π component series is expected to be more compressed than the σ component series, as is observed.

It is a pleasure for us to thank Professor J. R. Oppenheimer for several helpful discussions of points that arose in this problem.

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Surface and Volume Photoelectric Emission from Barium[1]

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Spectral sensitivity measurements between 5000 and 2300A have been made on barium surfaces prepared by fractional distillation in a gettered vacuum. The resulting yields are compared with those predicted by Mitchell's square-top barrier theory which is here modified to a form that facilitates comparison with experimental data. From 5000 to 3000A relative values of the observed yields are in good agreement with the modified theory. At 2967A there is an abrupt rise in the experimental curve which continues to the limit of the measurements. This is attributed to the onset of the volume photoelectric effect. The theoretical threshold for the volume effect calculated from the rough formulae of Tamm and Schubin agrees well with the experimental value.

It is usually assumed in the electron theory of metals that the electrons move independently in a periodic potential field in the metal. The introduction of a metallic surface which is necessary for the photoelectric effect gives rise to a second type of field and complicates the model by destroying the perfect periodicity of the crystal lattice. To avoid this difficulty Tamm and

[1] Presented in part at the Washington meeting of the American Physical Society, April 28–30, 1938.
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Schubin[3] proposed that the photoelectric emission from a metal should be regarded as arising from the superposition of two effects, the surface effect, due to the rapid change in potential at the surface, and the volume effect, due to the internal variations in potential. The argument is based on the fact that an electron in field-free space cannot absorb the energy of a photon and at the same time conserve both energy and momentum. They argue further that the threshold of the volume effect is considerably higher than the threshold for the surface effect since the possible transitions are restricted by a selection rule. The theory of the surface effect can then be simplified by using the Sommerfeld model in which the potential inside the metal is constant.

Experimental tests of the various theories of the surface effect over an extended range of wave-lengths have been confined in the past to observations on the alkali metals. If the theory of Mitchell[4] is taken as the most complete it may be concluded that experimental spectral distributions for the alkalies rise more abruptly and reach a maximum nearer the threshold than is predicted by the theory. In addition the theoretical curves are considerably flatter but the order of magnitude of the photoelectric yields is reasonably good.[5] In view of the rather discordant experimental results for the alkalies both for spectral and energy distributions it seems that more conclusive tests of the theory can be made on metals showing more consistent emission properties. This was the original purpose of the present investigation.

The experimental evidence for the volume effect has been extremely meager. Tamm and Schubin[3] considered the secondary rise which sometimes appears in the spectral distributions of the alkalies as evidence for the volume effect. The ease with which secondary peaks can be produced by contamination of the surface with vapors and gases would lead one to question at least some of these results. Experiments in the far ultraviolet have been carried out on other metals by Kenty,[6] the measurements extending as far as 584A. He found no maximum and subsequent secondary rise as the volume effect predicts. Very recently Baker,[7] working in the Schumann region with cadmium surfaces, has reported a second peak in the emission which he attributes to the volume effect. No attempt was made to work with thoroughly outgassed surfaces.

In the present investigation on spectral distributions, barium was chosen, first, because it possesses the lowest work function of any metal in the pure state with the exception of the alkalies, thereby permitting a wide frequency range, and second, since previous experiments in this laboratory[8] have shown that by using a special vacuum technique its emission properties are extremely stable and reproducible. In order to compare the results obtained with the theory of Mitchell[4] we have made certain simplifications in the theory which seem justifiable and obtain a result for the spectral distribution which may be readily applied to any metal.

Surface Photoelectric Effect

Modified Mitchell theory

The expression obtained by Mitchell (1934 paper, Eq. (83)) for the photoelectric current per unit power of incident radiation contains the frequency, threshold, and angle of incidence as well as the optical constants of the metal. The optical constants appear since the effect of reflection and refraction of the light has been included to prevent the emission from becoming infinite for grazing incidence and zero for normal incidence. The introduction of the optical constants into the theory may yield a more correct dependence of the emission on the angle of incidence but at present makes a critical test of the spectral distribution in this form improbable since very little is known experimentally of the variation of these constants with frequency for

[3] Tamm and Schubin, Zeits. f. Physik **68**, 97 (1931).

[4] K. Mitchell, Proc. Roy. Soc. **A146**, 442 (1934); **A153**, 513 (1936).

[5] The calculations of R. D. Myers, Phys. Rev. **49**, 938 (1936) and of A. G. Hill, Phys. Rev. **53**, 184 (1938) using an image field barrier show a maximum in the spectral sensitivity curve slightly nearer the threshold than the Mitchell theory with the square top barrier. L. I. Schiff and L. H. Thomas, Phys. Rev. **47**, 860 (1935), applied the quantum mechanical theory of the scattering of light by conduction electrons. This refinement also brings the maximum nearer the threshold, though the integral is too complicated for exact evaluation.

[6] Kenty, Phys. Rev. **44**, 891 (1934).

[7] Baker, J. Opt. Soc. Am. **28**, 55 (1938).

[8] Cashman and Huxford, Phys. Rev. **48**, 734 (1935); Jamison and Cashman, Phys. Rev. **50**, 624 (1936).

the desired range. An objection of fundamental importance is the fact that bulk metal optical constants are introduced into the theory of a surface phenomenon. The electrons exist originally in the force field at the surface but the constants of the light wave vary over a distance of the order of a wave-length into the metal. Consequently we consider only the incoming light wave without regard to the perturbation of the electric vector produced by the surface field with the realization that the dependence of the emission on angle of incidence will be incorrect but with the expectation that the form of the spectral distribution curve will be right. With this simplification the Mitchell theory for the square top potential barrier becomes

$$P_x=\frac{e^3\nu_a\sin^2\theta}{16\pi^5m^2c\cos\theta}\int_0^\infty\int_0^\infty\int_{\{\mu(\nu_a-\nu)\}^{\frac{1}{2}},\,0}^\infty \cdot\frac{4k_x^2\{k_x^2+\mu(\nu-\nu_a)\}^{\frac{1}{2}}}{\nu^4\{(k_x^2+\mu\nu)^{\frac{1}{2}}+[k_x^2+\mu(\nu-\nu_a)]^{\frac{1}{2}}\}^2} \cdot\frac{dk_xdk_ydk_z}{1+\exp h^2(k_x^2+k_y^2+k_z^2-\mu\bar{\nu})/8\pi^2mkT}, \quad (1)$$

where P_x is the emission per unit incident energy (e.s.u./erg), the k's the electron wave numbers associated with the x, y, and z directions, θ the angle of incidence, ν_a the frequency associated with the surface potential step, $\bar{\nu}$ the frequency associated with the width of the Fermi band at absolute zero, and μ a constant equal to $8\pi^2m/h$. In the k_x integration the lower limit is $\{\mu(\nu_a-\nu)\}^{\frac{1}{2}}$ if $\nu<\nu_a$ and 0 if $\nu>\nu_a$.

In order to evaluate (1) we introduce the cylindrical coordinates u, ρ and φ where u is the normal component of velocity. Then $k_x=(2\pi mu/h)$, $k_y=(2\pi m/h)\rho\cos\varphi$, $k_z=(2\pi m/h)\rho\sin\varphi$. Further let $\exp(m\rho^2/2kT)=Z$. Integrating with respect to Z and φ and letting $\frac{1}{2}mu^2+h(\nu-\nu_a)=kTy$, we have

$$P_x=\frac{B(kT)^2}{(h\nu)^4}\int_{0,\,h(\nu-\nu_a)/kT}^\infty \log[1+\exp(\beta-y)] \times\frac{(kTy+W_a-h\nu)^{\frac{1}{2}}(kTy)^{\frac{1}{2}}dy}{[(kTy+W_a)^{\frac{1}{2}}+(kTy)^{\frac{1}{2}}]^2}, \quad (2)$$

where

$$B=8e^3W_a\sin^2\theta/hc\cos\theta, \quad W_a=h\nu_a,$$
$$\beta=h(\nu-\nu_0)/kT, \quad \nu_a-\bar{\nu}=\nu_0,$$

the threshold frequency. Obviously kTy is the normal kinetic energy of the electron outside the metal. We now expand the fractional part of the integrand in powers of $(kTy/W_a)^{\frac{1}{2}}$ and (2) becomes, after converting to amperes per watt

$$P_x=\frac{B(kT)^2}{e(h\nu)^4}\sum X_m\int_0^\infty y^{\frac{1}{2}m}\log[1+\exp(\beta-y)]dy. \quad m=1,2,3,\cdots. \quad (3)$$

The quantities $h\nu$, W_a and kT are expressed in electron volts. Let $a=1-h\nu/W_a$ and $b=kT/W_a$ then $X_1=(ab)^{\frac{1}{2}}$, $X_2=-2a^{\frac{1}{2}}b$, $X_3=\frac{1}{2}(4a^{\frac{1}{2}}+a^{-\frac{1}{2}})b^{\frac{3}{2}}$, $X_4=-(a^{\frac{1}{2}}+a^{-\frac{1}{2}})b^2$, $X_5=(a^{-\frac{1}{2}}-a^{-\frac{3}{2}}/8)b^{5/2}$.

Integrals of the type represented in Eq. (3)

$$I_m=\int_0^\infty y^{\frac{1}{2}m}\log(1+e^{\beta-y})dy, \qquad m=0,1,2,3,\cdots$$

or its equivalent form

$$I_m=\frac{2}{m+2}\int_0^\infty\frac{y^{\frac{1}{2}m+1}}{e^{y-\beta}+1}dy$$

occur in many applications of the Fermi statistics to the electron theory of metals, and there has been need for a complete solution. Sommerfeld, Nordheim and others have given approximate solutions valid for negative or large positive values of β. Here we give complete solutions for all values of β:

For $\beta\leqq 0$:

$$I_m=\Gamma(\tfrac{1}{2}m+1)\sum_{s=1}^\infty\frac{(-1)^{s-1}}{s^{\frac{1}{2}m+2}}e^{s\beta}. \quad (4)$$

For $\beta>0$:

$$I_m=\frac{4\beta^{\frac{1}{2}m+2}}{(4+m)(2+m)} +2\sum_{k=0}^{l}\frac{m!!}{(m-4k)!!2^{2k}}C_{2k+2}\beta^{\frac{1}{2}m-2k}+R(m), \quad (5)$$

where the summation over k is extended to the largest integer l which gives a positive or zero power of β, depending on m. The constant C_{2k+2}

is defined by

$$C_{2k+2}=\sum_{s=1}^{\infty}\frac{(-1)^{s-1}}{s^{2k+2}}=\left(1-\frac{1}{2^{2k+1}}\right)\zeta(2k+2). \quad (6)$$

Values of the zeta function for real variables may be obtained from standard tables.[9] The remainder $R(m)$ is given as follows: if $\frac{1}{2}m$ is an integer,

$$R(m)=\pm(\tfrac{1}{2}m)!\sum_{s=1}^{\infty}\frac{(-1)^{s-1}}{s^{\frac{1}{2}m+2}}e^{-s\beta}, \quad (7)$$

where the $+$ sign is to be used if $\frac{1}{2}m$ is odd, the $-$ sign if $\frac{1}{2}m$ is even. If $\frac{1}{2}m$ is a half-integer:

$$R_m=[\tfrac{1}{2}m(\tfrac{1}{2}m-1)\cdots\tfrac{1}{2}]\sum_{s=1}^{\infty}\frac{(-1)^{s-1}}{s^{\frac{1}{2}m+2}}$$

$$\times\left\{\pi^{\frac{1}{2}}e^{s\beta}[1-\Phi([s\beta]^{\frac{1}{2}})]\pm 2e^{-s\beta}\int_0^{(s\beta)^{\frac{1}{2}}}e^{x^2}dx\right\}, \quad (8)$$

where the $+$ sign is used if $\frac{1}{2}(m+1)$ is an even integer, the $-$ sign if $\frac{1}{2}(m+1)$ is odd. In the latter case the remainder is usually negligible. $\Phi([s\beta]^{\frac{1}{2}})$ is the probability integral with limit $(s\beta)^{\frac{1}{2}}$. Tables of $\int_0^a e^{x^2}dx$ are available to $a=2$ (reference 9), and the integral may be calculated by an asymptotic expansion for large $a(=[s\beta]^{\frac{1}{2}})$ though the remainder $R(m)$ in this case is generally negligible.

The above solution of (1) holds well for the long wave-length side of the maximum of the spectral sensitivity curve (see Fig. 2) but the calculations become rather laborious for the short wave-length side since the convergence of (3) is not rapid for large β. Numerical integration for this region is easily carried out by noting that the integrand in (2) can be written

$$\log[1+e^{\beta-y}]\left(\frac{kT}{W_a}\right)^2\left[\frac{W_i}{kT}-(\beta-y)\right]^{\frac{1}{2}}$$

$$\times y^{\frac{1}{2}}\left[\left(y+\frac{W_a}{kT}\right)^{\frac{1}{2}}-y^{\frac{1}{2}}\right]^2,$$

where $W_i=h\bar{\nu}$. Hence the integrand can be split into two factors $f(y)$ and $F(\beta-y)$ and graphs of $f(y)$ against y and $F(\beta-y)$ against $(\beta-y)$ obtained. From these one gets $F\times f$ for a plot of the integral for any β.

[9] Cf. Jahnke-Emde: *Tables of Functions*.

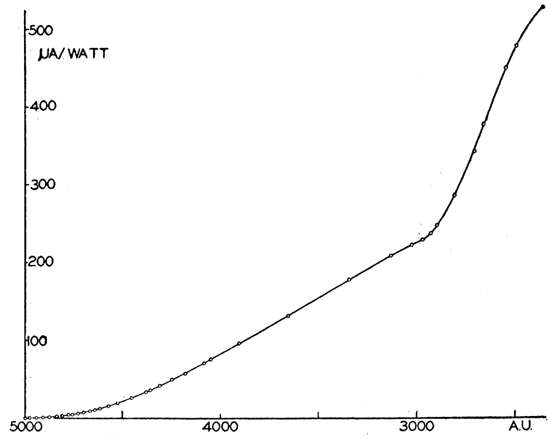

FIG. 1. Photoelectric yield for barium, for unpolarized light at approximately 60° incidence. $\varphi_0=2.49$ ev.

VOLUME PHOTOELECTRIC EFFECT

No calculations have been made to our knowledge of the emission as a function of frequency for the volume effect. Tamm and Schubin,[3] however, have made an estimate of the threshold position using the Bloch eigenfunction for electrons in the periodic field of a metal lattice. If it is assumed that there is one electron per atom, the lattice constant $a=n^{-\frac{1}{3}}$, where n is the number of electrons per unit volume. Their result for the volume threshold at absolute zero becomes

$$\nu_g=2(\nu_1\nu_a)^{\frac{1}{2}}-\nu_1 \quad \text{where} \quad \nu_1=4(\pi/3)^{\frac{2}{3}}\bar{\nu}. \quad (9)$$

EXPERIMENTAL TECHNIQUE

The construction of the phototube and the method of forming the barium surface were similar to that described in previous reports from this laboratory.[8] The envelope was made from a thin Corex D cylindrical blank whose ultraviolet transmission was previously determined. The barium was finally evaporated onto an outgassed movable nickel plate which served as cathode.

Optical system

The light sources employed were a tungsten filament lamp, a 110-volt Uviarc and an H3 high pressure Hg arc with the outer envelope removed. The radiation was focused by means of a quartz-flourite lens onto the entrance slit of a Gaertner monochromator whose exit slit had been removed. The dispersed radiation from this instrument was allowed to fall on a second Gaertner

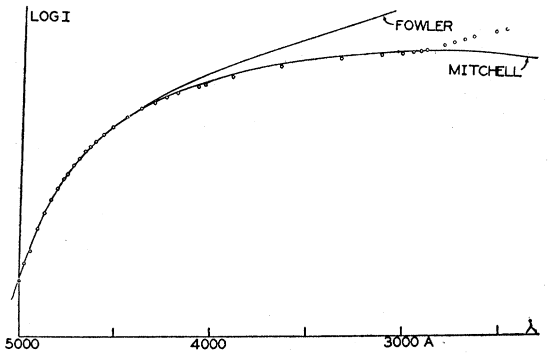

FIG. 2. Comparison of photoelectric yield from barium with theory. Circles are experimental values. Ordinates in arbitrary units. The maximum emission for the Mitchell theory is at 2720A.

monochromator of special design set in such a position that the entrance slit served as exit slit for the first instrument. The construction of the second instrument was such that its optical path was a mirror image of the optical path through the first instrument. The radiation from the exit slit was condensed by a special calibrated achromatic combination consisting of two quartz lenses, fixed to move in opposite directions to or from their optical center. Converging quartz lenses were placed against the entrance and exit slits of the second instrument so that the radiation from near the ends of the slits would not miss the lens which followed. This arrangement was particularly effective in the ultraviolet for increasing the energy output of the system. All slits were set at from 0.1 to 0.2 mm throughout the range of wave-lengths used. No scattered radiation could be detected.

Measurements of the energy of the resolved radiation were made with an improved form of Nichols radiometer[10] and with an evacuated Cartwright thermocouple. For the radiometric measurements an aluminum mirror was fixed about a vertical axis and mounted near the end of the condensing system. Rotation of the mirror through 90° served to expose alternately either the vane of the radiometer or the photoelectric surface to the radiation. With this arrangement the time between observations of photoelectric current and corresponding radiant energy was limited only by the period of the radiometer. For the thermocouple measurements it was found more feasible to mount the phototube beyond the end of the condensing system outside the principal focus and move the thermocouple in or out of the beam of radiation by means of a carriage mounted on a micrometer screw. Slit lengths were reduced to 3 mm so that the final image just covered the thermocouple junction. Measurements of the radiant energy could be made within a few seconds before or after the photocurrent measurement. A Leeds and Northrup galvanometer of sensitivity 5×10^{-8} volt/mm was used with the thermocouple and an FP 54 Pliotron in the circuit of DuBridge and Brown[11] served for the photocurrent measurements.

The thermocouple sensitivity was considerably enhanced by obtaining a low vacuum. To facilitate this the couple was pumped with a diffusion pump for several days and finally sealed off with a side tube containing outgassed barium in a tungsten spiral filament. Slow evaporation of the barium together with an occasional glow discharge in the side tube produced a vacuum which made the thermocouple extremely sensitive. Care must be exercised not to burn out the thermocouple wires during the glow discharge. The radiometer sensitivity was about ten times greater than that of the thermocouple-galvanometer combination but considerably more time was required to get readings due to the long period of the radiometer. This was objectionable when the arcs were unstable.

In obtaining a set of data by either method the monochromators were set at a particular wave-length and several consecutive readings made of the photocurrent and intensity of radiation. This procedure reduced the effect of arc fluctuations to a minimum. The two methods were in agreement within the limit of experimental error.

RESULTS

Measurements taken within an hour after the barium coating was formed and extending over a period of five months showed no observable changes with time in the emission as a function of frequency. The average of several runs is shown in Fig. 1 where the photoelectric yield in microamperes per watt has been plotted against wave-length. The work function for this surface as

[10] B. J. Spence, J. Opt. Soc. Am. 6, 625 (1922).

[11] DuBridge and Brown, Rev. Sci. Inst. 4, 532 (1933).

obtained by Fowler plots[12] is 2.49 ev. This value is 0.02 ev lower than that found by one of us[8] for barium deposited on glass. By reversing the electrode connections it was possible to draw electrons from barium deposited on the glass wall of the tube. This surface had the work function 2.51 ev, in agreement with the former value. This evidence together with previous results on the effect of heat treatment of the surface[8] leads us to believe that the small change in work function is attributable to slight differences in surface crystal structure rather than to gas contamination. Surfaces of a composite character or clean surfaces exposed to traces of gas show enhanced "temperature tails" on their spectral distribution curves and give the appearance of a metal emitting photoelectrons at a higher temperature. Fowler plots of the emission from such surfaces show response to wave-lengths several hundred angstroms longer than the threshold. These phenomena were not observed for the surfaces studied. The geometrical arrangement of the various elements of this phototube was such that the nickel plate would be appreciably heated by radiation during the deposition of the barium, whereas the glass wall was kept at room temperature. The coating on the nickel plate has the appearance of a finely etched surface but the coating on the glass is specular. There is considerable evidence in the literature from electron diffraction studies that a metal surface formed by condensation may have a preferential crystal growth depending on the backing surface and its temperature.

In comparing the results with the Mitchell theory (Fig. 2) we have plotted logarithms of the current because of the incorrect factor involving the angle of incidence[13] contained in Eq. (3). A vertical shift of the experimental points should superimpose them on the theoretical curve, log P_x *vs.* λ (Eq. (3)). The following constants were used in the theoretical equation: $kT=0.0259$, $h\nu_0=2.49$, $W_i=3.58$, $W_a=6.07$, all in electron volts. We have also shown in Fig. 2 the variation in theoretical current with wavelength as predicted by the simple Fowler theory.

[12] Fowler, Phys. Rev. **38**, 45 (1931).

[13] It is interesting that for $\theta=60°$ the theoretical current is about one-sixth the experimental current for the wavelength range 5000 to 3000A.

Discussion of Results

The curves of Fig. 2 show that the Mitchell and Fowler theories and the experimental points are in excellent agreement from 5000 to about 4300A. This does not necessarily mean that the square-top model is the correct one but only that the distribution of the surface electrons is that of Fermi since the exponential term in Eq. (1) dominates the variation in emission with frequency near the threshold. An image field type of barrier leads to results also in agreement with Fowler near the threshold.[14]

It is well to mention here that the effect of temperature on the emission at the threshold as predicted by Eq. (3) is no longer a T^2 relation as given by Fowler's[12] and DuBridge's[15] simpler theory but of the form $T^{5/2}(A-BT^{\frac{1}{2}}+CT-\cdots)$ where the work functions are considered constant. This would predict a temperature dependence of Ba slightly under $T^{5/2}$ at the threshold. This is nearer the Young and Frank ($T^{5/2}$) theory,[16] which is based on an approximation valid only near the threshold. The work functions themselves, however, are known to vary with temperature,[17] and this will alter the effective temperature dependence.

From 5000 to about 3000A the experimental data are in good agreement with the Mitchell theory (Fig. 2), a result which might not be expected in view of the rather arbitrary value assigned to the number of electrons per unit volume in calculating W_i. Here we have used 2 electrons per atom. Calculations by Wigner and Seitz[18] on sodium and by Hill[19] on beryllium indicate that for these metals the value is closer to 1. Fortunately the theoretical curve is rather insensitive to small changes in W_i. Fig. 1 shows that near the wave-length 2967A, in the region where the emission is beginning to flatten out, there is an abrupt rise which continues to 2345A, the limit of the measurements. This phenomenon we believe is unquestionably due to the onset of the volume effect. The theoretical curve reaches a peak in this region at 2720A. There are two

[14] K. Mitchell, Proc. Camb. Phil. Soc. **31**, 416 (1935).

[15] DuBridge, *Actualités Scientifiques et Industrielles* No. 268 (Paris).

[16] Young and Frank, Phys. Rev. **38**, 838 (1931).

[17] R. J. Cashman, Phys. Rev. **52**, 512 (1937).

[18] Wigner and Seitz, Phys. Rev. **43**, 804 (1933).

[19] A. G. Hill, Private communication.

reasons for believing that the experimental curve would also reach its maximum in this region were it not for the volume effect. First its slope continually decreases in the region 3129 to 2967A. Second, it will be observed that the slope of the experimental curve below 2600A decreases. One interpretation is that the supply of surface electrons diminishes for wave-lengths below about 2600A so that the total emission (surface and volume electrons) does not increase as rapidly for shorter wave-lengths. We believe, then, that the Mitchell theory with the modifications given above gives an adequate account of the variation in photoelectric yield with wave-length for the surface effect from barium.

In his 1936 paper Mitchell made certain refinements in the theory, designed to take into account surface roughness and lattice structure of the metal. The latter consideration would change the width of the energy band occupied by the conducting electrons at 0°K and hence change $\bar{\nu}$. Thus two parameters are introduced, ω and ν_0, whose values are adjusted to give the best fit to experimental data. The refined theory compared favorably with the results of Klauer[20] for clean potassium surfaces after an arbitrary choice of parameter values. It appears unnecessary to invoke these quantities in the present work, though an attempt to correlate the theory with the actual yield would undoubtedly require some factor involving the surface roughness.

The theoretical threshold for the volume effect obtained from Eq. (6) is 2950 or 3100A depending on the value assigned to $\bar{\nu}$ and hence ν_a. Because of the rough assumptions underlying the theory the agreement with the experimental value is satisfactory. The abrupt rise of the emission curve beyond the volume threshold is in marked contrast to the gradual rise after the surface threshold. The latter is dominated by the Fermi probability factor, rather than by the slowly varying excitation and transmission probabilities. The sudden rise in the curve for the volume effect should be explainable in terms of the transition probabilities between discreet energy zones. Another question of interest is the fraction of incident light energy available for the volume effect. Previous experiments[21] on Ba indicate that only $\frac{1}{3}$ percent of the incident light is absorbed by surface electrons. Hence practically all the light is absorbed by internal electrons, and thus one would expect an optimum theoretical yield of almost 50 percent were it not for secondary effects of scattering, re-emission, etc., which are estimated by Sommerfeld[22] to reduce the expected yield from the volume effect to about one percent.

A more complete theory of the spectral and energy distributions for the volume effect should be undertaken. Experiments are now in progress in this laboratory on the normal and total energy distributions for barium from the threshold to 2000A. It would be expected *a priori* that the energy distribution for the volume effect would be considerably different than for the surface effect. If it is possible to separate the two effects considerable information would be obtained about the actual energy states in the metal.

Acknowledgments

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[20] Klauer, Ann. d. Physik **20**, 909 (1934).

[21] Cashman and Jamison, Phys. Rev. **50**, 568 (1936).

[22] Sommerfeld, *Handbuch d. Physik* Vol. 24, No. 2, p. 472.