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New Aspects of the Photoelectric Emission from Na and K

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The external photoelectric effect for Na and K in the form of thick evaporated layers was investigated with photon energies $h\nu$ up to 6.71 ev. When $h\nu$ was within 1.5 ev of the threshold, the energy distributions of the emitted electrons were like those derived by DuBridge for a simple photoelectric effect involving an ideal metal. For larger $h\nu$, there was a growing preponderance of low velocity electrons. Their appearance could not be correlated, on the basis of a simple emission process, with the assumed parabolic shapes and approximately known widths of the valence bands. The following complications were therefore considered: (a) scattering by other electrons, causing the excited electron to lose energy before escape; (b) absorption of the recoil momentum by a second electron rather than by the entire crystal, resulting in the transfer of only a portion of the photon energy to the photo-electron; (c) modifications of the simple Fermi band by electron interactions, giving the effect of initial energy states much farther below the surface barrier than had been assumed.

The spectral distributions showed no evidence of a sharply defined "volume effect" such as might be due to optical transitions between zones. The form of these spectral curves was notably sensitive to variations in the structure of the evaporated films. Either matte or specular Na surfaces could be produced merely by controlling the deposition rate. There was no appreciable difference in the *energy* distributions for electrons from the two types of sufaces.

I. INTRODUCTION

PHOTOELECTRIC emission from metals has usually been treated as a simple process in which a single electron absorbs the full energy, $h\nu$, of a quantum, and appears outside the surface barrier with a kinetic energy

$$E=h\nu-(\mu-\epsilon)-\varphi. \tag{1}$$

Here ϵ is the total energy of the electron before excitation, μ is the Fermi level, and φ is the work function. (Both ϵ and μ are referred to the same arbitrary level.) To a first approximation, the excitation probability may be assumed independent of ϵ and $h\nu$. The probability that an excited electron will escape may be assumed proportional[1] to E. This elementary picture describes quite accurately the experimental results on metals when $h\nu$ is not too much greater than φ. Because intense sources of high energy photons were lacking, most observers in the past have confined their attention to this region relatively near the photoelectric threshold.

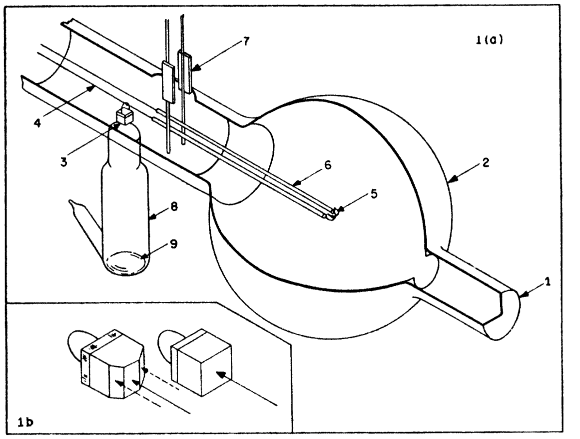

FIG. 1. (a) Cut-away sketch of photo-tube: (1) quartz window; (2) graphite coated collector sphere 6 in. in diameter; (3) movable bucket-type emitter; (4) tungsten hairpin; (5) bucket-support connected to hairpin; (6) sleeves of nickel tubing insulated from central hairpin by glass beading; (7) nickel armatures enabling one to pull spring-contact wires away from sleeves and shake buckets past; (8) last evaporation chamber, sealed off from rest of distillation train; (9) pool of alkali metal. (b) Bucket-shaped emitters drawn to a larger scale. They are shown in position for measurement, with arrows indicating the direction of the incident light. On the left is a glass bucket with polished facets allowing 0°, 45°, and 60° angles of incidence. (A strip of platinum paint on the glass around the top, and inside, provided conductivity.) On the right is a standard square metal bucket for which the angle of incidence is seen to be 0°.

For $h\nu > 5.0$ ev, the behavior of the photo-emission from the alkali metals can give an interesting check on the range of validity of the theories outlined above. These elements possess the lowest work functions known for pure metals, as well as the narrowest Fermi bands. For Na, the band width given by the Sommerfeld free electron model is about 3.0 ev, a value which has been corroborated by the soft x-ray emission work of Skinner[2] and of Cady and Tomboulian.[3] The work function of Na is about 2.3 ev. Thus, the lowest occupied state, in the simple band structure, lies below the vacuum potential by 5.3 ev. This is considerably less than the highest photon energies now in use.

If we denote by ϵ_1 the energy of an electron at the bottom of the conduction band, then $\mu-\epsilon_1=W$, the width of this band. For $h\nu$ greater than $\varphi+W$ in Eq. (1), we should expect to find no photo-electrons with kinetic energies smaller than $h\nu-(\varphi+W)$, since electrons obviously cannot originate in levels *below* the lowest occupied state.

The shape as well as the width of the Fermi band might be expected to influence the form of the energy distributions. In an ideal metal, the density of states rises as $(\epsilon-\epsilon_1)^{\frac{1}{2}}$. According to Mitchell[4] and to Makinson,[5] the excitation probability at the bottom of the

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[1] The original assumptions of Fowler and DuBridge are treated in slightly modified form by Apker, Taft, and Dickey, Phys. Rev. **74**, 1462 (1948).

[2] H. W. B. Skinner, Trans. Roy Soc. (London) **239**, 95 (1940).

[3] W. M. Cady and D. H. Tomboulian, Phys. Rev. **59**, 381 (1941).

[4] Mitchell, Proc. Roy. Soc. (London) **146A**, 442 (1934).

[5] Makinson, Proc. Roy. Soc. (London) **162**, 367 (1937).

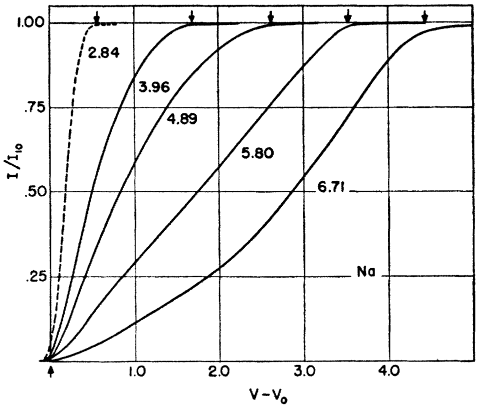

FIG. 2. Current-voltage characteristics for Na with $h\nu=2.84$, 3.96, 4.89, 5.80, and 6.71. Currents are normalized with $I=1.0$ at applied voltage $V=+10$ volts. The curves are set coincident at V_0, the stopping potential for 0°K. No reverse-current corrections were necessary. The position of V_s, the voltage required for saturation of the photo-current, is marked by an arrow in each case. The corresponding value of the work function of this particular Na surface is 2.27 ev.

band is approximately proportional[6] to $(\epsilon-\epsilon_1)$. Let us again take the escape probability proportional to E. Then for the specialized case in which $h\nu$ is just sufficient to eject electrons from the lowest state, $E=(\epsilon-\epsilon_1)$. The resultant energy distribution would rise as $E^{5/2}$. This should apply to the emission from Na at $h\nu\sim 5.3$ ev. The relative sparsity of slow electrons so indicated was not found in the experiments described here. In fact, just the opposite of this trend was observed.

As one might have surmised, the theory of the preceding paragraphs is not nearly complex enough to account for the behavior of the photo-emission from Na and K when $h\nu-\varphi$ is greater than about 1.5 ev. In a later section, some possibilities will be suggested to explain the large percentages of low velocity photo-electrons obtained.

II. EXPERIMENTAL DETAILS

Most of the methods and apparatus used in this experiment have been described in previous papers.[7] Figure 1 is a sketch of a typical photo-tube showing the features of chief interest. The collecting sphere was coated with a graphite-bentonite mixture and thoroughly baked, first in nitrogen, then in high vacuum. Each alkali metal was subjected to four or five preliminary distillations before being sealed (at a pressure of about 5×10^{-7} mm Hg) into $\frac{1}{2}$-in. diameter Pyrex pellets. These were broken in vacuum by glass-sheathed nickel armatures, and further distillation was carried out in a Pyrex evaporation train connected directly to the photo-tube. The metal was finally deposited on the movable bucket-type emitters when the last evaporation chamber was gently torched. This was done in the sealed-off tubes at pressures ranging from 2×10^{-8} to 4×10^{-7} mm Hg.

With an emitter in place for measurement, an arbitrary potential could be applied between it and the insulated sleeves of the supporting hairpin. This compensated for the difference in the work functions of the sleeve material and the emitting surface. As illustrated in the first paper of reference 7, results may be distorted seriously by stray fields if this point is ignored.

In four separate photo-tubes, 24 Na surfaces were prepared on buckets of Ni, Ta, Pt, Ag, and glass. For K, only one tube was constructed; Ni, Ta, and Pt served as substrates for the 4 surfaces investigated.

III. RESULTS

Figure 2 shows retarding-potential curves for the photoelectric emission from Na with values of $h\nu-\varphi$ ranging from about 0.5 to 4.4 ev. The corresponding energy distributions are given in Fig. 3. For $h\nu=3.96$ the results resemble the parabolic current-voltage characteristic and linear energy distribution predicted by DuBridge's simple theory. However, for $h\nu$ near 5.0 ev, there is no suggestion that the energy distributions rise as $E^{5/2}$. (Note that kinetic energy increases to the *left* in Figs. 2 to 5.) Moreover, for $h\nu>5.3$ ev the minimum photo-electron energy is zero, not $h\nu-(\varphi+W)$ as mentioned in the introduction. Also, photo-electrons with energies close to zero are much more numerous than was expected.

Measurements on Na with accelerating potentials up to 900 v gave more evidence of the importance of slow

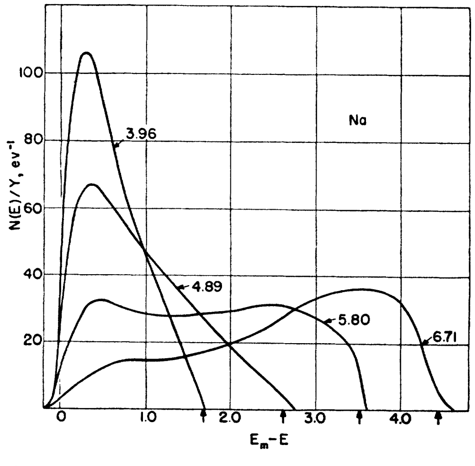

FIG. 3. Energy distributions, $N(E)/Y$, obtained by differentiating four of the curves in Fig. 2. (Y represents the yield in electrons per quantum. As defined in reference 1, $N(E)$ implicitly contains the factor Y. Hence, the differentiation of *normalized* current-voltage curves gives $N(E)/Y$.) The ordinate scale is given in percent normalized current per electron volt. Zero on the abscissa scale corresponds to the maximum kinetic energy (E_m) at 0°K. Energies *decrease* toward the right, and the arrows mark the points at which $E=0$ for each value of $h\nu$.

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[6] For electrons near the top of the conduction band, there is no great error involved in assuming the excitation probability independent of ϵ, as in the first paragraph of this section. The larger W, the smaller this error.

[7] Apker, Taft, and Dickey, Phys. Rev. **73**, 46 (1948); **74**, 1462 (1948); Taft and Apker, Phys. Rev. **75**, 344 (1949); J. A. Becker, Elec. Eng. **68**, 937 (1949).

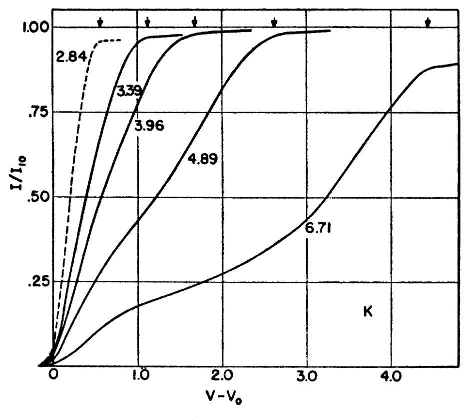

FIG. 4. Current-voltage characteristics for K, presented in the same manner as the curves for Na in Fig. 2. Corrections have been made for back currents amounting to five to eight percent of I_{10}. Values of $h\nu$ are indicated beside each curve. The dotted characteristic was included to show the fairly sharp saturation point which determined the work function (2.27±0.03) of this *K* surface.

photo-electrons for $h\nu > 5.0$ ev. For values of $h\nu$ from 2.84 to 4.89, the percentage increase of photo-current at 900 v (over that at 10 v) became steadily lower, in the manner typical of a simple Schottky effect. For higher $h\nu$, the slopes of the saturation curves became steeper, thus indicating the collection of greater numbers of electrons emerging with extremely low kinetic energies.

Curves analogous to those for Na are shown for K in Figs. 4 and 5. Again we find increasingly higher percentages of low energy electrons as $h\nu$ becomes larger. (The results are distinguishable from those of Na because of the fairly large fraction of the electrons that retain energies within 0.5 ev of the maximum ($E_m = h\nu - \varphi$) even when $h\nu = 6.71$ ev.)

Energy data taken at six values of $h\nu$ in addition to those listed confirmed the existence of the effects already described for both Na and K; for the sake of clarity, these results are not presented in the figures.

Before the spectral distributions are discussed in detail, a short description of the results of various evaporation techniques may be of value. Layers of Na deposited rapidly (in a few minutes) were smooth and shiny; if the substrate was well polished, the deposit was specular. On the other hand, slow evaporations (requiring 15 minutes or more) produced very white, frosty deposits which did not show metallic luster.[8]

Shiny surfaces invariably gave a smooth spectral distribution with no appreciable maximum. An example of this is the lower curve (*B*) in Fig. 6, taken on a specular film of Na on Ta. In contrast, there was a pronounced maximum in the distribution of the yield from frosty surfaces. This is shown by curve *A* in Fig. 6, taken on a very white sparkling deposit of Na on Ta.

The ordinary type of bucket, in position for measurement, presents a flat emitter surface normal to the incident light beam. If this surface were extremely smooth, there would be only a very small component of the electric vector perpendicular to the emitting areas. With faceted buckets as sketched in Fig. 1(b), spectral distributions were taken for shiny Na with unpolarized light at various angles of incidence. Although the yields at angles of 45° and 60° were as much as 3 or 4 times higher than those at 0°, the maximum in the spectral distribution obtained for shiny surfaces in this manner was broader and lower than the peak of curve *A* in Fig. 6. Since contamination had raised the work function of these surfaces to about 2.5 ev, the experiment did not give a conclusive answer to the question of whether the high maximum found for frosty Na on flat buckets was entirely due to the high angles of incidence at which light struck the elemental emitting areas of the matte surface.

A reproducible feature of the data for shiny Na deposits on the faceted emitters is shown in the inset of Fig. 6. For light incident at 0° the curve continued downward as $h\nu$ increased to 6.19 ev, but at 45° and 60° the yields went through a minimum at $h\nu \cong 5.7$ ev. The same minimum was found in the spectral distributions

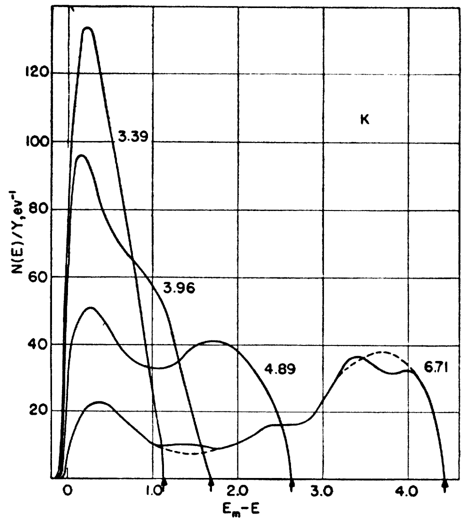

FIG. 5. Energy distributions for K, obtained by differentiating the curves in Fig. 4. Because of low yield, data at $h\nu = 6.71$ are not as trustworthy as those at other values of $h\nu$. The dotted sections of this energy distribution show ,results obtained on another K surface. The corresponding current-voltage curve is not given in Fig. 4.

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[8] No correlation was noted between pressure (as read by the ion-gauge) during evaporation and the formation of either type of Na surface. Likewise, the phenomenon seemed to be indifferent to the substrate except in one instance: all attempts to evaporate frosty Na on previously deposited layers of shiny Na were unsuccessful; the reverse process was easily carried out for sufficiently heavy layers, however. In all cases, the substrates were at room temperature, except for heating effects due to condensation of the Na atoms or to radiation from the warm evaporator bulb. These effects were greater during the fast evaporations, of course.

A pertinent paper dealing with the influence of evaporation rates on the formation of thin metal films has been published recently by R. S. Sennett and G. D. Scott, J. Opt. Soc. Am. **40**, 203 (1950).

for *all* the frosty surfaces, whatever the angle of incidence.[9]

The results on matte Na are in reasonable agreement with those described by Maurer,[10] although the surfaces were not as stable. Contamination shifted the threshold to higher *hν* values and lowered the yields slightly. Curve *A* of Fig. 6, was taken on a surface only 45 minutes old. Except for a shift of about 0.1 ev to the right, it compares fairly well with Maurer's "Na D" spectral distribution shown in Figs. 4 and 5 of his paper.

Hill's[11] energy-distribution for Na at 2536A ($h\nu = 4.89$), showing a relative abundance of slow electrons, is in agreement with the results examined in the first paragraph of this section. The minor deviations from simple theory which he found for smaller values of *hν* can probably be attributed to a contact potential difference between the spherical emitter and its supporting rod.

That optical effects can account for most of the differences between the spectral distributions for shiny and for frosty Na surfaces is supported by the fact that energy distributions at a given value of *hν* for the two types of Na were nearly the same. Shiny surfaces consistently yielded a slightly smaller percentage of slow electrons than did frosty surfaces. (All energy data were taken with an angle of incidence of about 0°.) Contamination or aging effects were much less noticeable on the current-voltage curves than on the spectral distributions. The curves of Fig. 2 were all taken within 5 minutes to 2 hours after deposition of a frosty surface.

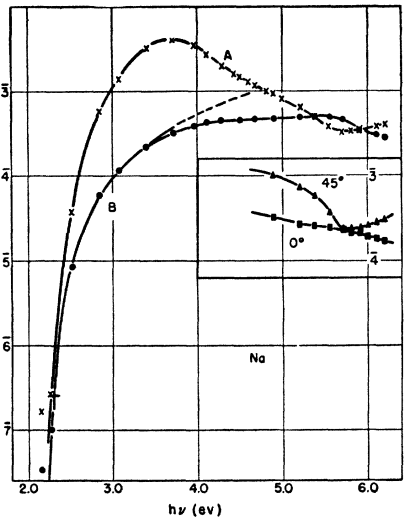

FIG. 6. Spectral distributions of the photoelectric yield from Na. (The characteristics of the logarithms of the yield are negative.) Curves *A* and *B* were taken with unpolarized light (at 0° angle of incidence with the polished Ta substrates) on matte and specular deposits, respectively. Fowler's theoretical distribution (dotted curve) fits the lower characteristic for about 1.0 ev near the threshold, giving a work function of 2.30. In the inset are shown sections of two spectral distributions taken on a shiny surface of Na on glass with unpolarized light at the two angles of incidence indicated. Note that the ordinate scale here has been shifted down one decade, but that the abscissa scale is unchanged.

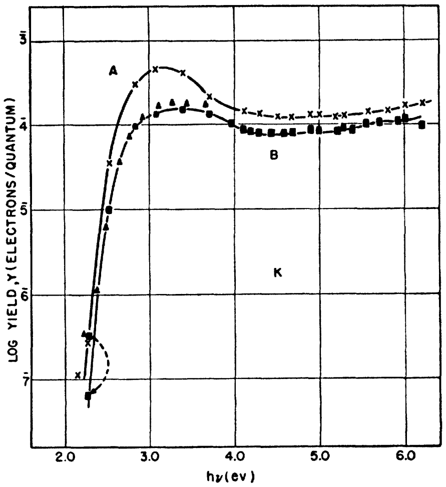

FIG. 7. Spectral distributions of the photoelectric yields from two slightly different surfaces of K on Ni (see text). Unpolarized light at 0° angle of incidence was used in each case. The triangles on the lower curve represent data taken with a tungsten lamp immediately after deposition of the K. All other points were taken with a 1-atmosphere mercury arc. The intensity of the source of 6.71-ev radiation was not accurately known, so no yields are given for this value of *hν*. The dotted arrow shows the decrease in yield at $h\nu = 2.27$ when a suitable bias-voltage suppressed photo-current caused by scattered light striking the thin film of K on the sleeves of the bucket support.

The spectral distributions for K, given in Fig. 7, are for uniform matte surfaces on flat metal buckets with incident light normal to the substrate. K layers which looked rather frosty immediately after deposition acquired a shiny even-textured graininess in a few hours. Curve *A* was taken on the frostier of the two surfaces represented here. It is similar in shape to Klauer's[12] spectral distribution for a fresh K deposit; his highest value of *hν* was 3.39 ev. His yields were given only in order of magnitude; the estimate was 10^{-4} electrons/quantum or less, at the peak, which occurred at a slightly lower value of *hν* than that for the maximum in curve *A*. Contamination effects in the K tube were of the same type as those described for Na. Surfaces produced under the best vacuum conditions had work-functions of ∼2.20. This is a slightly lower value than the one given in Fig. 4, and is probably closer to the value for clean K.

Tentative values of the photoelectric yields for Rb were about the same as those for K, and the spectral distributions showed the same slight maximum and minimum as seen in curve *B* of Fig. 7.

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[9] Increasing the angle of incidence from 0° to 70° on frosty surfaces almost doubled the yields but did not change the general shape of the spectral distributions.

[10] R. J. Maurer, Phys. Rev. **57**, 653 (1940). The writer is indebted to Dr. Maurer for a more detailed description of his method of depositing Na.

[11] A. G. Hill, Phys. Rev. **53**, 184 (1938).

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

IV. CONCLUDING REMARKS

The outstanding effect observed in this experiment was the rising proportion of slow photo-electrons emitted by Na and K as $h\nu$ was increased. The maximum photon energy (6.71) was more than 1 ev in excess of that required to eject electrons from the lowest levels of the valence bands described by the Sommerfeld model. Energy distributions of the emitted electrons for values of $h\nu > 4$ ev were markedly at variance with the results predicted by simple theories. Some possible reasons for the discrepancies are set down briefly in the following three paragraphs.

An excited electron may lose energy by collisions with other conduction electrons. The probability that the scattered electron will escape from the surface increases with the amount by which $h\nu$ exceeds the work function. The applicability of DuBridge's analysis to the energy data at low $h\nu$ must depend on the fact that few of the scattered electrons appear externally when

$$h\nu - \varphi < 1.5 \text{ ev.}$$

A photo-electron may acquire considerably less than the entire energy of an exciting photon because a second electron, instead of the crystal as a whole, receives the recoil momentum.[13]

The actual distribution of the initial energy states doubtless differs somewhat from the ideal parabolic form that has been assumed. The extent to which electron interactions may alter the simple picture is difficult to assess accurately.[14] It is conceivable that levels near the bottom of the conduction band are broadened by a phenomenon analogous to the Auger effect described by Skinner.[2, 15] The low energy tail on the soft x-ray emission spectrum represents a decidedly smaller deviation from the ideal band shape than would be necessary for a complete explanation of the photoelectric results on Na, however.

It should be noted that the three mechanisms discussed separately above are probably not independent. The interrelations and similarities which may exist will not be considered here.

In the case of a metal with a slightly higher work function and wider Fermi band, it seems likely that the simple photoelectric effect should account for most of the yield in the range of $h\nu$ considered here. Skinner's experimental value of the band width W for Li is about 4.0 ev. A Li surface of work function $\varphi = 2.6$ ev was prepared by E. A. Taft of this laboratory. Tentative energy distributions of the photo-electrons at $h\nu = 6.7$ ev showed a considerably lower percentage of slow electrons than found for Na and K at the same $h\nu$. This strengthens the supposition that complicating effects play a less prominent part in the photo-emission when $h\nu \leqq \varphi + W$.

The spectral distributions are presented as subsidiary data. Their behavior was quite dependent on the physical structure of the evaporated surfaces; this was presumably due to differences in the optical properties of the various types of deposits. Thus it seems hazardous to try to correlate any features illustrated in Figs. 6 and 7 with factors influencing the form of the energy distributions.

The spectral data gave no clearcut evidence of a "volume effect" like that discussed by Tamm and Schubin.[16] One might expect such a phenomenon to produce an increase in yield starting at some critical frequency dictated by the zone scheme of the metal.[17] This type of effect need not show up at all in the energy distributions. It would not give rise to a disproportionate number of slow photo-electrons unless the allowed transitions were especially probable for electrons near the bottom of the conduction band. Even this possibility does not account for the many electrons which appear to come from *below* the bottom of the simple Fermi band.

Except in the case of shiny surfaces struck by light at normal incidence, the Na spectral distributions showed a definite but very gradual upward slope in the range of $h\nu$ from 5.7 to 6.2 ev. An estimate of the intensity of the 6.71-ev source indicated that the total yield was still increasing with $h\nu$ at this point. Photoelectric experiments can give few clues as to the reasons for the increase. It might be ascribed to a change in the excitation probability with frequency, to an increased escape probability of the scattered electrons, or to the variation of optical constants.[18] Judging from the results shown in the inset of Fig. 6, one concludes that none of these effects makes an important contribution to the yield when the electric vector is *parallel* to the emitting surface.

I am very much indebted to Drs. H. A. Bethe, H. Brooks, M. H. Hebb, and H. B. Huntington for their interest in discussing the theoretical problems involved in this work. I wish to express my sincere thanks to Dr. L. Apker for encouragement and advice, and to Mr. E. Taft for experimental assistance.

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[13] This mechanism was proposed by Dr. Harvey Brooks and Professor H. A. Bethe in helpful discussions for which the writer is very grateful.

[14] E. Wigner, Trans. Faraday Soc. **34**, 678 (1938).

[15] See P. T. Landsberg, Proc. Phys. Soc. (London) **A62**, 806 (1949) for a theoretical treatment of this problem. E. P. Wohlfarth [Phil. Mag. **41**, 534 (1950)] finds that Landsberg's approach can also be used successfully in the theory of the specific heat of Na.

[16] Tamm and Schubin, Z. Physik **68**, 97 (1931).

[17] H. Y. Fan concludes from his calculations [Phys. Rev. **68**, 43 (1945)] that the volume effect should become important not far from the threshold of the surface photoelectric effect.

[18] According to Wood [Phys. Rev. **44**, 353 (1933)], Na becomes transparent at $h\nu \sim 5.9$, K at $h\nu \sim 3.9$.