Photoelectric Properties of Bismuth*

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(Received October 22, 1941)

Photoelectric threshold determinations with Fowler plots were made for six bismuth surfaces evaporated on glass under high vacuum conditions. The values obtained for the work function were all between 4.22 and 4.25 ev. There was no significant temperature variation over the range −70°C to 200°C for the wave-length 2537A, but the data indicated contamination at the lower temperatures. Values of the parameter α, the number of electrons that strike unit area of the surface per second and absorb a quantum of energy when the light intensity is unity, were obtained for the bismuth surfaces and found to be 0.03 to 0.1 as great as those of sodium surfaces investigated by Maurer. Like those of sodium, the values of α are $\sim 10^{-2}$ as great as the upper limit set by DuBridge if the number of free electrons per bismuth atom is assumed to be five.

INTRODUCTION

BECAUSE of the unusual structure of the electronic bands in metallic bismuth, an investigation of its photoelectric properties is of interest.[1] Early work on partially outgassed bismuth surfaces was done by Parmley.[2] Rentschler and Henry[3] determined the threshold wave-length to be 2870A, corresponding to a work function of 4.31 ev. More recently, Weber[4] investigated some of the photoelectric properties of thin bismuth films, making threshold determinations by the temperature variation method of DuBridge.[5] A limiting value of about 2600A with increase of film thickness was obtained. Since the completion of the work described in this paper, Weber and Eisele[6] have reported additional data on bismuth films and an apparent threshold wave-length of about 2785A.

EXPERIMENTAL

Photo-currents were measured with FP-54 tubes in DuBridge-Brown and Barth circuits. The light intensity was measured by a sodium cell calibrated against a thermopile-galvanometer system having a sensitivity of about 4×10^{-8} watt per cm deflection. The sodium surface in the cell was a thick matte layer deposited on nickel and was checked for linearity of response and constancy of yield over the surface. The light sources were a low pressure mercury arc and a zinc-neon arc resolved with a Bausch and Lomb single quartz monochromator. The amount of scattered light was negligible and background was corrected for by running over the spectral

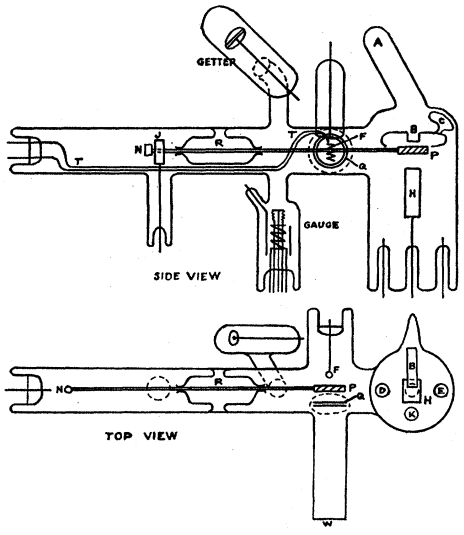

FIG. 1a. Bismuth photo-cell.

* Part of this work was presented as a section of a dissertation presented to the Faculty of the Graduate School of the University of Rochester in candidacy for the Degree of Doctor of Philosophy, June, 1940.

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[1] Fowler plots for Be, Mg [M. M. Mann, Jr. and L. A. DuBridge, Phys. Rev. **51**, 120 (1937)], Ba (R. J. Maurer, *Photoelectric and Optical Properties of Sodium and Barium*, (Thesis, 1939)), and W [A. H. Warner, Phys. Rev. **38**, 1871 (1931)], for which metals the electronic bands are known to overlap (H. M. O'Bryan and H. W. B. Skinner, Phys. Rev. **45**, 370 (1934); F. Seitz, *Modern Theory of Solids* (McGraw-Hill, 1940)), show no irregularity due to an overlapping band structure. The overlap is known to be small in the case of Be and large, about 1.5 vol ts, in the case of Mg.

[2] T. J. Parmley, Phys. Rev. **30**, 656 (1927).

[3] H. C. Rentschler and D. E. Henry, J. Opt. Soc. Am. **26**, 30 (1936).

[4] A. H. Weber, Phys. Rev. **53**, 895 (1938).

[5] L. A. DuBridge, Phys. Rev. **39**, 108 (1932).

[6] A. H. Weber and L. J. Eisele, S. J., Phys. Rev. **59**, 473A (1941).

line to find the maximum and minimum of the photo-currents measured in the neighborhood of a line, interpolating and subtracting. The monochromator was mounted on a heavy iron base which turned upon ball bearings to allow convenient shifting from photo-cell to thermopile.

Figures 1a and 1b show the first bismuth photocell constructed. The tube was baked out and all the metal parts with which the bismuth would come in contact were heated to a bright red to clean them before the bismuth was inserted. The cell was cracked at the small tube *A* and the bismuth dropped into the tantalum tray *B*. The glass was then baked twice at 500°C for an hour and the metal parts outgassed before and after the second bake-out. The tray *B* could be turned to a vertical position and the bismuth melted down into the tantalum trough *H*. The bismuth did not wet the tantalum. This trough could be heated by passing a current through the leads *K* and *L*, evaporating the bismuth on a flat polished glass plate, *P*, sealed to a tungsten rod which slid through the inner glass support *R*. The glass plate could then be moved back in front of the quartz window by a magnetic pull on the nickel slug *N*. *J* was a V-shaped tantalum sheet embracing the tungsten rod and providing electrical contact. The collector *Q* was made of two loops of tantalum wire.

The bismuth was Hilger spectroscopic bismuth, 99.998 percent pure. This purity was checked by a chemical analysis by Dr. J. F. Flagg of the Chemistry Department. The pressure in the tube, measured by means of an ionization gauge, was about 2×10^{-8} mm Hg after sealing off from

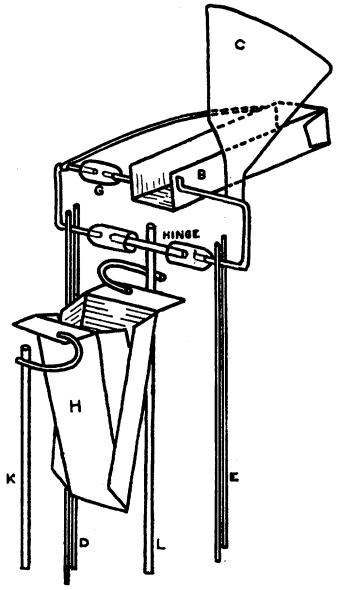

FIG. 1b. Bismuth photo-cell, evaporation assembly.

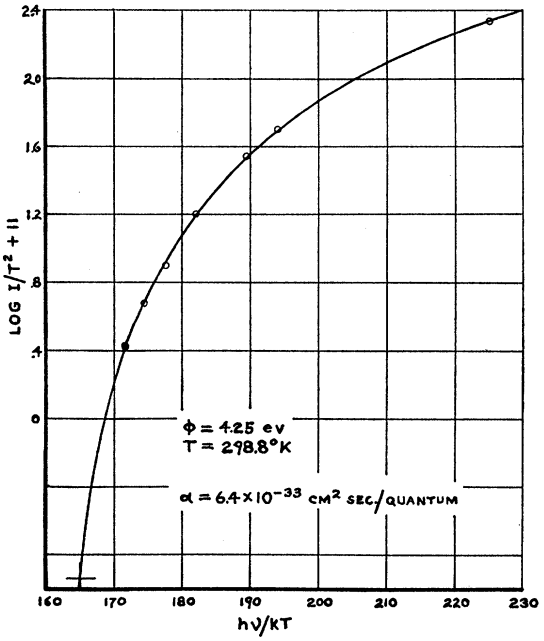

FIG. 2. Fowler plot for bismuth surface 1.

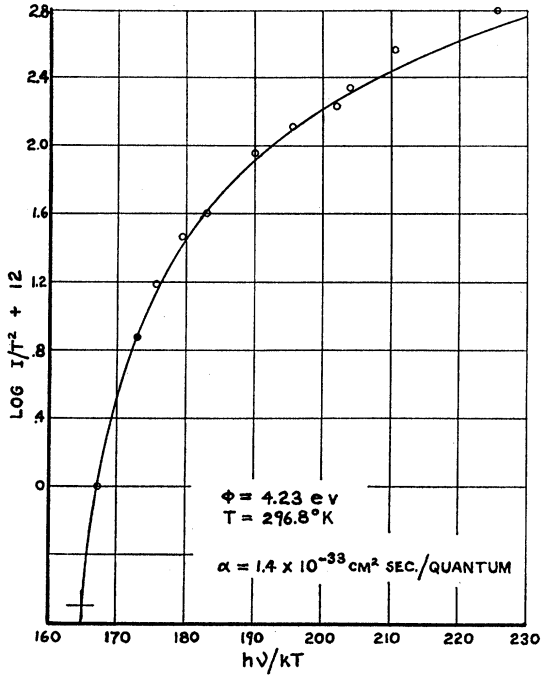

FIG. 3. Fowler plot for bismuth surface 4.

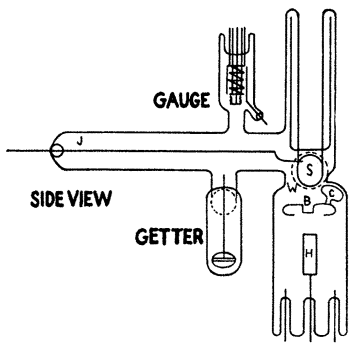

FIG. 4. Bismuth photo-cell.

the pumps. Sections of the photo-cell were thoroughly torched after baking and before sealing off to remove any invisible layers of bismuth from the glass walls. The trough H was outgassed at a bright red heat and the bismuth kept molten in B at about 500°C at the same time before sealing off. The bismuth was transferred from the tray to the trough after the tube was off the pumps. It is estimated that the trough was heated to about 650°C in order to evaporate the bismuth on P.

The ionization gauge was also used to indicate pressures when the surfaces were being formed. The first two surfaces were deposited at pressures of about 3×10^{-7} mm Hg and the last two more slowly at about 5×10^{-8} mm Hg. The pressure returned quickly to 2×10^{-8} mm after the deposition of each surface. The first bismuth surface evaporated was opaque and formed a mirror, but as successive layers were put down, the surface became more matte and grayer in appearance. Since the yield from all the bismuth surfaces varied from point to point by about 25 percent when a narrow slit image was used, a circular spot, 6 or 7 mm in diameter, of parallel light was used, and care was taken to illuminate the same area of the bismuth surface. Figures 2 and 3 show the Fowler plots obtained from data taken on surfaces 1 and 4 within a few hours after deposition.

The second photo-tube was constructed in order to check results obtained with the first tube and also, in view of Weber's results of films, to attempt to take temperature variation data. The evaporation assembly remained the same, but (Fig. 4) the bismuth was evaporated on a polished glass surface s inclined at 45°. The skirt on the re-entrant tube carrying s insulated it from the rest of the tube, and bismuth deposited on the inner walls of the tube formed the collector. Glycerin placed in the re-entrant tube and heated electrically and a dry-ice alcohol slush were used in the temperature variation runs. A Chromel-Alumel thermocouple was placed in the bath with the tip against the back of s. Corrections to the temperature readings were made by using the value of the heat conductivity of Pyrex quoted by Getting and Leighton[7] and assuming a value of 0.3 for the emissivity of bismuth. An estimated error of 2°C was made in determining the temperature of the bismuth surface. These surfaces were also evaporated at pressures of about 5×10^{-8} mm Hg. Only two surfaces were investigated in the second tube, and only Fowler plot data were taken on the first surface. Figures 5 and 6 show the Fowler plot for these two surfaces designated as I and II.[8] The line $\lambda=2537$A was used to illuminate surface II as the temperature was varied from 200°C to −70°C.

RESULTS AND DISCUSSION

The values of the work function from Fowler plots of four surfaces in the first photo-cell were 4.25, 4.25, 4.23, and 4.23 ev. A Fowler plot for surface 2 taken 24 hours after the first set of data showed a shift of the work function to

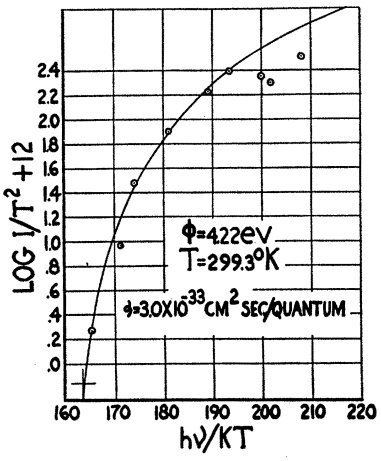

FIG. 5. Fowler plot for bismuth surface I.

[7] I. A. Getting and H. W. Leighton, Rev. Sci. Inst. **11**, 232 (1940).

[8] The lack of agreement, in general, between the theoretical Fowler curve and the experimental points corresponding to wave-lengths shorter than the 2480A line of the Hg arc is not significant here because of the difficulty in measuring the intensity of these Hg lines.

4.27 ev. A second set of data on surface 4 two weeks later yielded the result 4.24 ev. Surface 4 was then heated to 150°C by radiation from the filament F in an unsuccessful attempt to take temperature variation data, and the work function determined several days after this treatment was 4.31 ev. The values of the work function of the two surfaces deposited in the second photocell were 4.22 and 4.23 ev.

The yields for the surfaces 1 to 4 decreased successively. The values of α for surfaces 1 and 4 were, respectively, 6.4 and 1.4×10^{-33} cm^2 sec. per quantum. For surface I, $\alpha=3.0\times10^{-33}$ cm^2 sec. per quantum. Values of α obtained by Maurer[1] for two sodium surfaces were 5.0 and 3.3×10^{-32}. DuBridge[9] obtained the upper limit to the value of α given by

$$\alpha=h^3/2\pi mu^2=(2m/\pi h)(8\pi/3n_f)^{4/3}=1.51n_f^{-4/3},$$

where u is the Fermi energy, m is the electron mass,[10] and n_f is the number of free electrons per unit volume. Observed values of α for Be, Mg, Na, W, and Ba range from 10^{-2} to 10^{-3} times the DuBridge upper limit if all the valence electrons are assumed to be free.[11] If the number of free electrons per atom of sodium is taken to be one, if the difference in atomic weight and density is taken into consideration, and if the ratio of the α for sodium to that for bismuth is 10, the number of free electrons per atom of bismuth calculated from the ratio obtained by using the last expression for α is approximately five. It is known that the measured values of optical constants of metals for a frequency large compared with that for which internal photoelectric absorption takes place give a value of the effective number of free electrons equal to the number of valence electrons. The behavior of the electron as though free at high frequencies is contained in the quantum theory of the optical properties of metals.[12] Data taken by Meier[13] on a polished

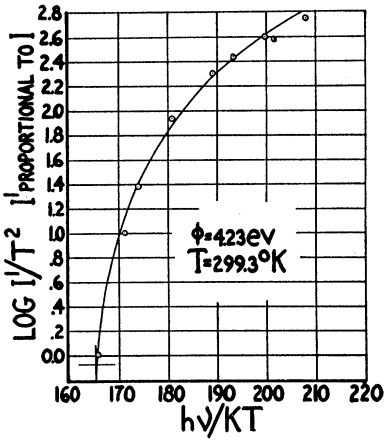

FIG. 6. Fowler plot for bismuth surface II.

bismuth surface suggest an absorption peak in the infra-red, and if classical theory is used, 2.3 free electrons per atom may be calculated from the absorption coefficient and index of refraction at 2500A. It may be expected that a polished surface absorbs more strongly than a crystalline surface[14] and that optical constants of crystalline bismuth would give a greater value for the effective number of free electrons.

Since the spectral distribution curves show no variations that can be ascribed to the electronic band structure, it is interesting to compare Fowler theory with approximate results obtained by a simple consideration of one of the existent pictures of the electron bands in bismuth. It has been shown that the significant Brillouin zone (the fifth) contains almost five electrons per atom, and data indicate that about 10^{-4} electron per atom overlap into the next zone.[15] Jones[15] has been able to account for galvomagnetic effects in bismuth by regarding the energy surfaces of the

[9] L. A. DuBridge, *New Theories of the Photoelectric Effect* (Hermann and Cie., Paris, 1935).

[10] The m that occurs in the denominator of the first expression for α may be considered the mass of an ejected electron. To obtain the second form, the normal electron mass is substituted in the expression for the Fermi energy, not the effective mass.

[11] M. M. Mann, Jr. and L. A. DuBridge, Phys. Rev. **51**, 120 (1937).

[12] R. de L. Kronig, Proc. Roy. Soc. **A124**, 409 (1929).

[13] W. Meier, Ann. d. Physik **31**, 1017 (1910).

[14] Mott and Jones, *Properties of Metals and Alloys* (Oxford Press, 1936), p. 116.

[15] H. Jones, Proc. Roy. Soc. **155**, 654 (1936); Mott and Jones, *Properties of Metals and Alloys* (Oxford Press, 1936). Jones deduced the magnitude of the number of overlapping electrons per atom from both the change of sign of the temperature coefficient of resistance and the magnetic anisotropy of the bismuth-tin alloy system. The assumption is made that each bismuth atom that is replaced by a tin atom carries with it one of the electrons from the overlapping region. The amount of overlap of the two bands is determined by this value of the number of overlapping electrons. Since the electron carried away may come from a region of the lower band not overlapping the upper band and may have a higher effective mass or even normal mass, the number of overlapping electrons and therefore the amount of overlap of the two bands may be greater than the value given by Jones. However, the order of magnitude of the results in the following sections would probably remain unchanged.

electrons lying outside the fifth zone and those of the positive holes in the fifth zone as very eccentric ellipsoids. The surfaces of constant energy for n electrons per unit volume lying outside the fifth zone in k space are given by

$$E_1=(h^2/2m)(\alpha_1k_x^2+\alpha_2k_y^2+\alpha_3k_z^2)$$

and for n positive holes per unit volume in the fifth zone in k space are given by

$$E_2=\text{const.}-(h^2/2m)(\beta_1k_x'^2+\beta_2k_y'^2+\beta_3k_z'^2).$$

Measurement of the magnetic susceptibility parallel and perpendicular to the principal axis of bismuth do not permit the evaluation of the β's but indicate that the ellipsoid describing E_2 is more eccentric than that describing E_1. These data, together with measurements of the temperature coefficient of resistance of the tin-bismuth alloy system, yield the result that $\alpha_1=\alpha_2\sim40$ and $\alpha_3\sim1$, where $m/\alpha_{1,2,3}$ may be taken as the effective mass of an electron and the subscripts 1, 2 refer to a direction perpendicular and the subscript 3 refers to a direction parallel to the principal axis of a bismuth crystal.[16] The energy interval between the bottom of the second zone and the surface of the Fermi distribution is

$$E=(n_0/3)^{\frac{2}{3}}(\alpha_1\alpha_2\alpha_3)^{\frac{1}{3}}(h^2/8m)(3/\pi\Omega_0)^{\frac{2}{3}}\sim0.23 \text{ ev},$$

where Ω_0 is the atomic volume and n_0 is the number of overlapping electrons per atom. The electron velocities perpendicular and parallel to the principal axis are given by

$$v_x=v_y=(n_0/3)^{\frac{1}{3}}\alpha_1^{\frac{1}{3}}(\alpha_1\alpha_2\alpha_3)^{\frac{1}{3}}(3/\pi\Omega_0)^{\frac{1}{3}}h/2m\sim v_f,$$

$$v_{||}=(n_0/3)^{\frac{1}{3}}\alpha_3^{\frac{1}{3}}(\alpha_1\alpha_2\alpha_3)^{\frac{1}{6}}(3/\pi\Omega_0)^{\frac{1}{3}}h/2m \sim10^{-\frac{2}{3}}v_f\sim0.2v_f,$$

where $v_f=(3/\pi\Omega_0)^{\frac{1}{3}}h/2m=$velocity of a free electron.

The number of electronic states per unit volume of bismuth with energy between E_1 and

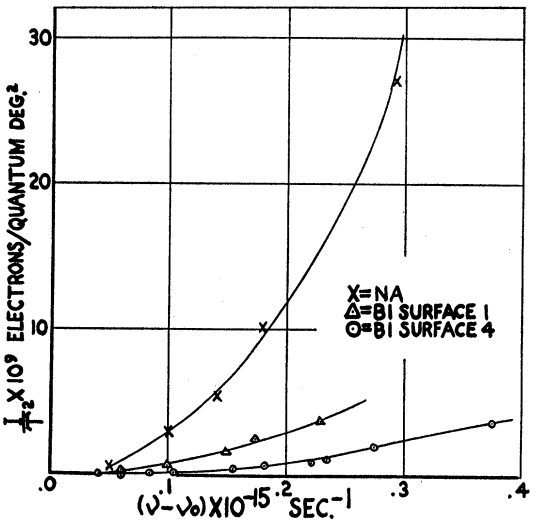

FIG. 7. Spectral distribution curves for sodium and for bismuth.

dE_1 is given by

$$N(E_1)dE_1=(1/4\pi^2)(8\pi^2m/h^2)^{\frac{3}{2}}E_1^{\frac{1}{2}}dE_1/(\alpha_1\alpha_2\alpha_3)^{\frac{1}{2}}$$
$$=(\alpha_1\alpha_2\alpha_3)^{-\frac{1}{2}}N(E_f)dE_f,$$

where $N(E_f)dE_f$ is the distribution in energy obtained from the Sommerfeld model of a free electron gas and corresponds to the Fermi-Dirac distribution at 0°K. Let $I(\nu)$ be the photo-current emitted for unit incident light intensity of frequency ν. If the density of states is given by const. $E^{\frac{1}{2}}dE$ and the electron velocity is given by const. v_f, then following the DuBridge derivation of the Fowler equation corresponding to 0°K, one obtains that $I(\nu)=$const. $[h(\nu-\nu_0)]^2$, where ν_0 is the threshold frequency. If the DuBridge argument about the upper limit to the yield is applied to a model having the density of states given by

$$(\alpha_1\alpha_2\alpha_3)^{-\frac{1}{2}}N(E_f)dE_f=\alpha_1^{-1}N(E_f)dE_f$$

and having $\sim10^{-2}$ electron per atom of effective mass $m/40$ and with all velocity components equal to those of free electrons, then the order of magnitude of this upper limit to the yield remains the same as when five free electrons per atom are considered. A model having $\sim10^{-4}$ electron per atom of normal mass and with velocity components ~0.2 those of free electrons would, if the density of states is again given by $\alpha_1^{-1}N(E_f)dE_f$, give an upper limit about ten times greater than

[16] M. Blackman [Proc. Roy. Soc. **166**, 1 (1938)] investigated the low temperature magnetic susceptibility of bismuth and explained the fluctuating magnetic susceptibility by a model in which $\alpha_1=9.8$, $\alpha_2=1$, $\alpha_3=1.1\times10^3$, and the amount of overlap is 0.019 ev. The number of free electrons per atom computed from this overlap is 1.2×10^{-5}, but Blackman points out that the number of electrons responsible for the fluctuations probably is much smaller than the number determining the high temperature susceptibility.

the former limit. Near the top of the almost filled band the distribution in energy is given by

$$N(E_2)dE_2=(1/4\pi^2)(8\pi^2m/h^2)^{\frac{3}{2}} \times(\text{const.}-E_2)^{\frac{1}{2}}dE_2/(\beta_1\beta_2\beta_3)^{\frac{1}{2}},$$

where the const. in the root is the highest energy in the band. The previous arguments concerning the photo-currents applied to a density given by const. $(E_{\max}-E)^{\frac{1}{2}}dE$ lead to

$$I(\nu)=\text{const.}\ (h(\nu-\nu_0))^2.$$

In view of this and of the rough estimate of what could happen to the value of the DuBridge upper limit to the yield, although temperature effects are not taken into consideration, it is not too surprising that the spectral distribution of the photo-electric yield fits the theoretical Fowler plot near the threshold. If the photo-current is plotted as a function of the difference between the incident and threshold frequency for surfaces 1 and 4 and for a sodium surface investigated by Maurer, Fig. 7 is obtained. A detailed investigation of the yield in a frequency range corresponding to the overlap of the energy bands could not be undertaken at room temperature with the Hg arc. A tendency for the bismuth atoms to form small groups of definite orientation when the surface is being formed might explain the variation in yield from point to point on a surface, but there is no proof that this was the case.

As the temperature of surface II was lowered from 200°C to room temperature, the photo-electric current remained constant to 2 percent when the surface was illuminated by the line $\lambda=2537$A. When the dry-ice alcohol bath was placed in the re-entrant tube and the surface allowed to warm up to room temperature, the yield again remained constant but at a value lower than that obtained during the higher temperature portion of the run. This lower constant value was observed as the surface was again warmed up slightly above room temperature, and a Fowler plot taken at room temperature indicated a shift of the threshold to shorter wave-lengths and therefore probable contamination by gases adsorbed when the surface was cold. The curve $\log I/T^2$ *versus* $\log I/T$ obtained if the yield is assumed constant in the temperature range −70°C to 200°C is a straight line. Comparison with the theoretical curve then gives only the information that the threshold is less than or equal to about 4.44 ev. Weber's earlier determination[4] of the limiting value of the long wave-length threshold with increasing film thickness corresponds to a work function of about 4.75 ev. The observed data fit both the positive and negative branches of the theoretical curves in the temperature range −53.8°C to 24.4°C, but not for higher temperatures. Films possibly contaminated by gas and films more carefully protected showed little difference. In the later work,[6] the temperature range was extended to liquid-air temperatures,[17] and the long wave-length limit obtained corresponded to a work function of about 4.47 ev.[18] The work function reported here agrees more nearly with that obtained of Rentschler and Henry.[3]

Grateful acknowledgement is made of the advice of Dr. L. A. DuBridge during the course of this work.

[17] This temperature was reported in the presentation of the paper mentioned in footnote 6.

[18] *Note added in proof.*—A. H. Weber and L. J. Eisele, S. J. [Phys. Rev. **60**, 570 (1941)] found it impossible to fix an upper limit to the threshold wave-length of bismuth films from the results of more recent work. The DuBridge method yielded the somewhat uncertain threshold 3125Å.