PHOTO-ELECTRIC THRESHOLD OF SINGLE BISMUTH CRYSTALS

By T. J. Parmley

Abstract

A bismuth single crystal grown by Bridgeman's method was mounted in a specially constructed, highly evacuated bell jar. By means of external magnet control it was possible to cut the specimen along a crystal face and advance it into position in a Faraday cylinder. *Photo-electric current fatigue curves* were taken for the 2537A line under three different vacuum conditions. It was found that the fatigue was smaller, the higher the vacuum. The long wave-length limit was determined by plotting the current per unit intensity as a function of the wave-length of the mercury arc used. The threshold was determined under the two following conditions: first, after the new surface had aged an hour in a vacuum of the order of 10^{-6} mm; and second, immediately after cutting a new face in a vacuum of the order of 10^{-7} mm. The two values were 2567A and 2835A respectively. Similiar observations on the poly-crystalline form yielded the values, 2560A and 2830A. Experiment showed that the threshold changed rapidly from 2835A to 2567A in the low vacuum. It was found that this shift was not due to oxygen, nitrogen, or carbon dioxide, the chief constituents of air, but to some other source of contamination which was not located.

Introduction

It has been recognized for some time that many of the discrepancies in the values of the photo-electric threshold, or long wave-length limit of a metal, are directly attributable to a contamination of the metal by its surrounding atmosphere. Attempts to minimize this factor are seen in the investigations of Richardson and Compton,[1] and Hamer[2] in which the surface was cleaned in air and quickly placed in the evacuating vessel. In this way the possibility of contamination was decreased. Presumably the ideal thing would be to perform all the operations in such a high vacuum that there could be little doubt as to the cleanliness of the metal surface. Recently this has been accomplished by Millikan,[3] Kasda,[4] Kadesch and Hennings,[5] and Tucker[6] with very significant results.

In the present investigation, surfaces of single and polycrystals of bismuth were prepared in vacuum in order that reliable thresholds for these forms might be obtained. Bridgeman's method[7] was followed in making the single crystals. The details of cutting the specimens and making observations are fully discussed in the following pages.

[1] Richardson and Compton, Phil. Mag. **24**, 576 (1912).
[2] Hamer, Optical Soc. of Am. J. **9**, 251–257 (1924).
[3] Millikan, Phys. Rev. **7**, 355–388 (1916).
[4] Kazda, Phys. Rev. **26**, 643 (1925).
[5] Kadesch and Hennings, Phys. Rev. **7**, 147 (1916).
[6] Tucker, Phys. Rev. **6**, 574–581 (1923).
[7] Bridgeman, Proc. Amer. Acad. Sci. **60**, (Oct., 1925).

Apparatus

Fig. 1 shows a longitudinal section of the apparatus. The specimen S was so mounted that the 0001 plane was perpendicular to the paper and parallel to the lines in the diagram. It was attached to the sliding mechanism NRO which could travel back and forth horizontally in the trough T. O is a piece of quartz tubing for insulation purposes; N is a cylindrical piece of soft iron which is moved by an external coaxial electromagnet.

With the razor blade C raised, the specimen could easily be moved into positions C and S. The cylinder of soft iron H, magnetically operated, was used both as a lifting device for the blade and as a hammer. H and G are separate so that if H was raised a distance less than the length of L the blade was not raised. Through this distance, then, H was used as a hammer without

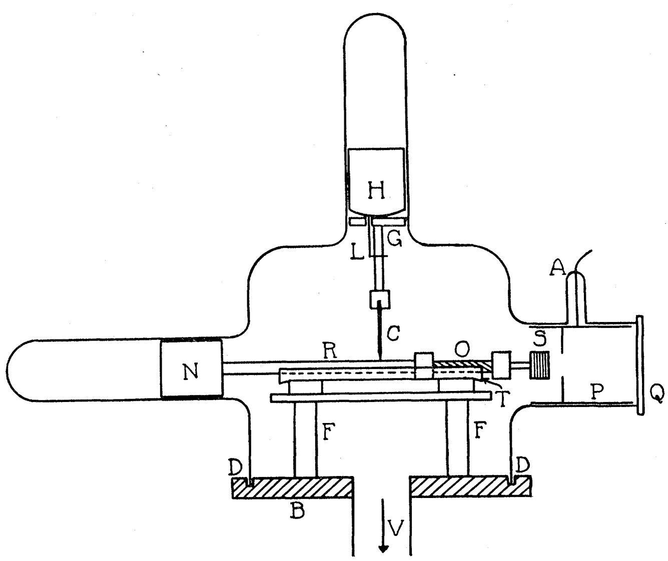

Fig. 1. Longitudinal section of apparatus.

disturbing the position of the blade. If it was desired to move S, H was raised still higher.

With the exception of the blade and bell jar, all the mountings were made of brass. A brass tube which was soldered in the hole in B fitted snugly over the glass tubing that connected the bell jar to the evacuating vessel. De-Khotinsky cement was used here, at D, and at Q.

The system was evacuated by a two stage mercury diffusion pump in series with a Cenco Hyvac pump. Pressures were measured with a McLeod gauge graduated to 0.005 microns. A liquid air trap was inserted in the system between the pumps and the bell jar to prevent mercury vapor diffusing into the latter vessel. During part of the experiment a charcoal trap with the usual liquid air bath was placed between the previous air trap and the glass vessel.

A Bruleur Galloi's quartz mercury arc lamp[8] served as a source of illumination, and monochromatic radiation of a desired wave-length was directed upon the specimen by means of a quartz monochromator. In all cases the slits of the monochromator, which were only 0.1 mm wide, were much narrower than those used by previous investigators. The particularly strong source of illumination made this fine adjustment possible. Throughout the experiments the lamp was run at 84 volts and 2.80 amperes.

The specimen S was connected by a platinum wire through the walls of the glass vessel to an electrometer. The electrons ejected from the metal were pulled to the Faraday cylinder P by a positive potential of about 45 volts. The rate of drift of a spot of light on a scale reflected from the mirror of the instrument was taken as a measure of the photoelectric current. The electrometer had a sensibility of 1500 mm per volt.

To determine the long wave-length limit, the photoelectric currents per unit intensity of the incident light were plotted as ordinates and the wave-lengths as abscissas. The extrapolated intercept on the wave-length axis gave the value of the threshold.

The relative intensities of the lines of the mercury arc lamp after passing through the quartz monochromator were measured by means of a linear thermopile and a Coblentz galvanometer. The results of these measurements are given in the following table:

Wave-length (A)	2400	2483	2537*	2652	2754	2804	2894
Intensity	15.5	31.1	100.0	75.4	14.2	35.2	19.9

*Arbitrary standard

Experimental Results

Previous to making photoelectric measurements, the pumps were run for several hours with the liquid air trap but not the charcoal trap in the system. Then the specimen was cut and moved into its final position as shown in the cross-sectional drawing. It was under these conditions that the data for the fatigue curve (decay of the photo-electric current with time) I of Fig. 2 were obtained. The current decreased very rapidly in the first twenty minutes and then changed less rapidly, becoming almost constant after an hour.

Because of the very rapid decay of the photo-electric current with time it was impossible to determine the exact value of the threshold for the clean surface. It was found, however, that the threshold must lie between the two lines 2894A and 2804A. Within approximately ten minutes after beginning observations the surface was insensitive to the 2804A line. In other words, the threshold had shifted beyond this line to shorter wave-lengths. It was after an hour's fatigue when the current became quite constant that the first determinations of the threshold were made as shown in curve III of Fig. 3. The threshold for the single crystal was 2560 ± 10A; for the polycrystal, 2567 ± 10A. The ordinate values in this case are given on the right

[8] Gallois mercury lamp, Revue D'Optique **4,** 89 (1925).

side of the graph. The pressure in the bell jar during these observations was of the order of 10^{-6} mm.

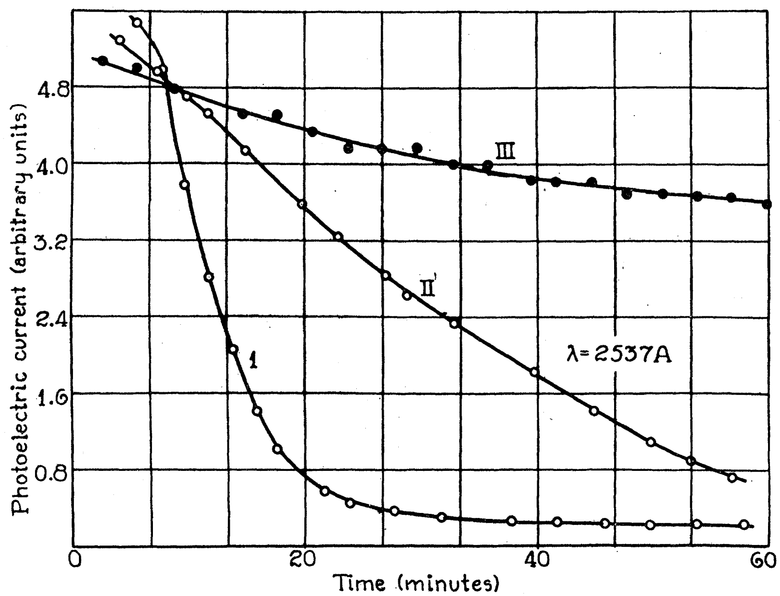

Fig. 2. Decay of photo-electric current with time.

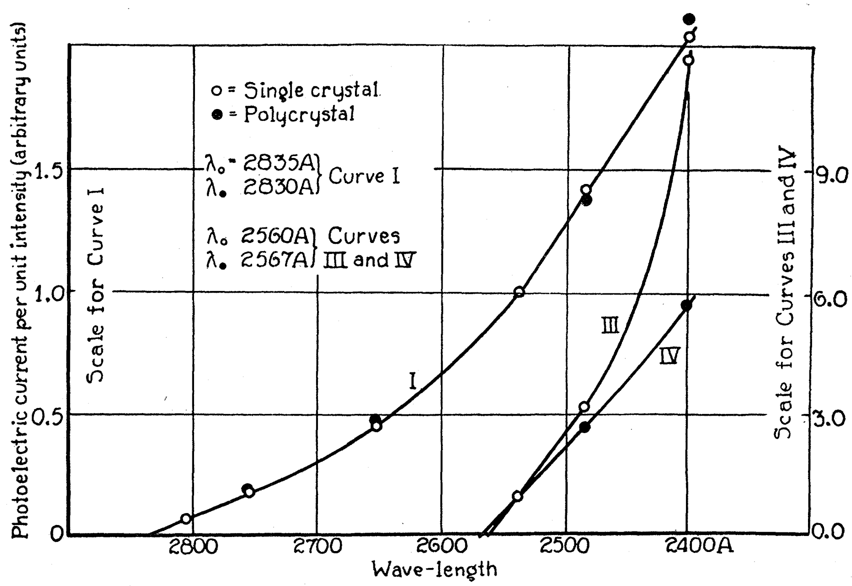

Fig. 3. Curves showing the photo-electric threshold.

With an increasingly good vacuum in the system the fatigue curves changed into curves II and III of Fig. 2. Curve II is the result of a cocoanut charcoal trap in the system in addition to the liquid air trap; curve III is the result of prolonged running of the pumps under the conditions of the last curve. In this case the pressure in the system was of the order of 10^{-7} mm.

It was under conditions similar to those stated for curve III, Fig. 2, that the thresholds for the single and polycrystals of bismuth were determined. With the two traps in the system and after prolonged running of the pumps, the specimen was cut, advanced into its position in the Faraday cylinder, and the proper readings of the photo-electric current taken (Curve I, Fig. 3). The threshold for the single crystal was 2835 ± 10A; for the polycrystal, 2830 ± 10A.

In the hope of discovering the cause of the drift in the threshold oxygen, nitrogen, and carbon dioxide were each in turn introduced into the system and readings of the photo-electric current due to the 2652A line taken over a period of an hour. In each case before starting the experiment the system was washed repeatedly with the gas in question. The gas was at a pressure of about 1 mm while readings were being made. Under these conditions the crystal was cut and the surface illuminated by the 2652A line. In each case it was found that the threshold was above the 2652A line.

Discussion

The following conclusions can be drawn from the above experiments. First of all the three characteristic fatigue curves I, II, III, represent conditions of increasingly good vacuum. Curve I is the result of only a liquid air trap in the evacuating system; curve II is the result of a liquid air trap plus a charcoal trap; and finally, curve III is the result of the conditions of II plus prolonged running of the pumps. Clearly then, the higher the degree of vacuum the less the fatigue. This suggests that in a perfect vacuum no fatigue would take place, a conclusion already drawn by several other investigators.

The fact that the thresholds of the single crystal and polycrystal forms of bismuth are practically the same is rather surprising inasmuch as the thermal and electrical conductivities of the single crystal are different for different axes. Nevertheless, the experimental result indicates that the work to take an electron through the metal surface is the same regardless of the face. This function which Richardson[9] has shown is equal to the thermionic work function $\phi(=V)$ can be readily calculated. If we should substitute in the equation

$$Ve = h\nu_0 = hc/\lambda_0,$$

$e = 4.77 \times 10^{-10}$; $h = 6.55 \times 10^{-27}$; $c = 3.00 \times 10^{10}$ cm/sec; and λ_0 (for the single crystal) $= 2835$A, we find a value for V of 4.36 volts.

A comparison of the results of this experiment with those of previous investigations of the threshold of bismuth may possibly clear up some of the discrepancies found in the literature. Pohl and Pringsheim[10] and Werner[11]

[9] Richardson, Science N. S. **54,** 283 (1921).

[10] Pohl and Pringsheim, Deutsch. Phys. Gesell. Verh. **13,** 480 (1911).

[11] Werner, Upsala Universitets Arsskrift (1914).

used accelerating potential methods, while Richardson and Compton[12] and Hughes[13] used stopping potential methods. A brief discussion of their results is given below.

A rather serious criticism can be offered to Pohl and Pringsheim's work. They had only three points with which to determine their curve, and one of these was very doubtful. The third point not indicated on the curve (Fig. 4) is at 3130A where a very weak current was detected. It seems that there is a great likelihood that this effect might have been due to stray light and not to the 3130A line at all. The possibility that stray light could have been present in their system is suspected from the shape of the curve. Most curves of this type cut quite sharply into the wave-length axis, but this one tails

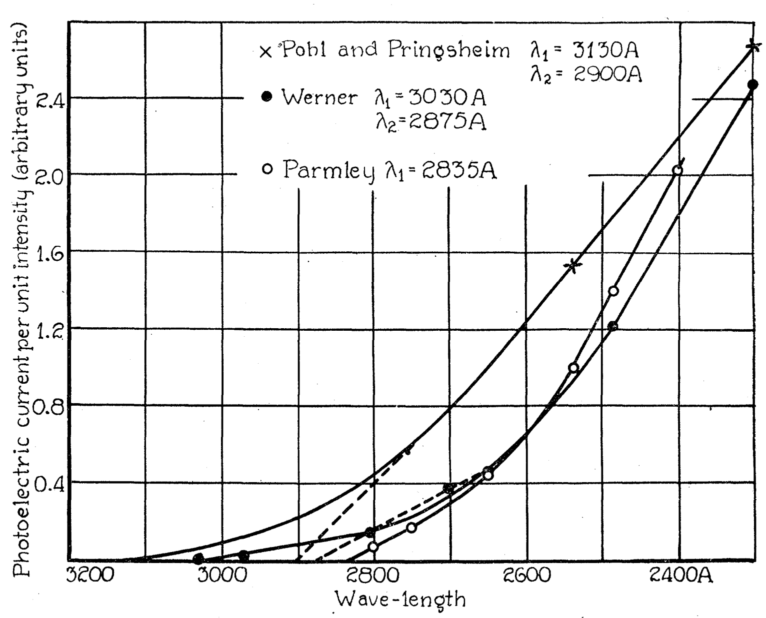

Fig. 4. Comparison of threshold curves with those of other observers.

off to the left. If one takes the liberty of dotting in what seems to be a more reasonable curve, one gets the extrapolated value of 2900A. This value is probably nearer the true threshold than that given by Pohl and Pringsheim.

Werner's results are given in his curve in Fig. 4. As can be seen he has a much more defined curve than that of Pohl and Pringsheim, but it has the same excessive bending to the left near the foot. This throws doubt on the values indicated by the last two points. They represent small currents which might have been due to stray light. The dotted line in this case gives a value for λ_0 of 2875A.

One other criticism might be offered. Since the procedure of preparing the surface necessitated a reasonably low vacuum for sputtering, contamina-

[12] Richardson and Compton, Phil. Mag. **24,** 576 (1912).
[13] Hughes, Phil. Trans. Roy. Soc. **212,** 205–226 (1912).

tion of the bismuth was possible before readings were taken. At no time during Werner's experiments was the pressure much below 0.1 mm.

Because Richardson and Compton used an entirely different method (retarding potential method) of determining the threshold, it is not possible to make as many specific criticisms as in the above cases. However, there is at least one point that could have been improved upon. This is contained in the following statement. "The metal strip to be tested was carefully scraped with a clean knife blade. It was then placed quickly into position and the vacuum pump started." This suggests the possibility of contamination taking place before any readings were made. If all this could have been done in vacuum, the results might have been very different. Richardson and Compton's value for λ_0 was 3370A.

Hughes used a very ingenious method of preparing a clean metal surface in vacuum and at the same time eliminating troublesome surface films. However, his method had the undesirable feature that it was impossible to perform all the operations in a high vacuum. Hughes' value for λ_0 was 3233A.

In reviewing the four methods just discussed one thing should be noted. The value of λ_0 in each of the cases is greater than that given in this paper. This might be explained in the light of Tucker's work,[14] who found that as he denuded a platinum foil of its gases by heating, he was able to push the threshold farther and farther into the ultra-violet. He concluded, however, that there is a limiting value for λ_0 when all the gases had been driven off. If this same reasoning can be applied to the work on bismuth, it would mean that the single crystals broken in vacuum were freer from contamination than any of the other surfaces prepared.

The present paper also gives a second value for the threshold of bismuth under conditions differing from the first. In this case, the charcoal trap was disconnected from the system and the surface was allowed to age for an hour before readings were taken. Very probably a gradual contamination took place during this time even though a fairly good vacuum was maintained by means of the pumps and liquid air trap.

At first it was naturally assumed that a bismuth oxide had been formed with a corresponding change in the threshold. This seems rather doubtful in the light of the experiment in which oxygen was purposely introduced into the system. Unfortunately the experimental work on this point was not extensive enough to determine whether the oxygen caused any shift in the original threshold. The results did show, however, that after a two hour period the threshold was still above the 2652A line. Evidently, oxygen was not the particular agent which caused the marked change in the threshold of the bismuth. Nitrogen and carbon dioxide, the other chief constituents of air, were successively tried with similar results. Since then in a fairly high vacuum this shift in the threshold does take place and since it apparently does not take place in atmospheres of oxygen, nitrogen, or carbon dioxide,

[14] Tucker, Phys. Rev. **6**, 574–581 (1923).

one must conclude that the contaminating agent is other than those mentioned.

Two possible sources of contamination can be mentioned: first, all seals were made with De-Khotinsky cement; and second, zinc chloride was used as the flux in soldering the bismuth to the moving brass system. If some component of these two was the responsible agent, one can readily see that in a good vacuum it would be a much more important factor of contamination where diffusion would be fairly rapid than in an atmosphere of one of the three gases at a pressure of 1 mm where diffusion would be slow. This could explain why the 2652A line remained active after such a long period of time as found in the latter experiments. This point of view is indirectly supported by the recent work of Dunn[15] who found that even in a high vacuum the threshold of stagnant mercury changed from 2735A to 2850A and after several days dropped to 2680A due to a contamination which he could not definitely locate. Evidently, there is quite a field for investigation on this point.

I take this occasion to express my appreciation to Professor Tucker for suggesting this problem, and to Professors Merritt and Collins for their helpful suggestions during the investigation.

Rockefeller Hall,
Cornell University,
July 1, 1927.

[15] Dunn, Phys. Rev. **29**, 693 (1927).