THE PHOTO-ELECTRIC RESPONSE OF POTASSIUM AT LOW TEMPERATURES

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ABSTRACT

Variation of photo-electric currents from potassium with temperature, 20° to −180°C, for the visible spectrum.—Carefully purified potassium in a highly evacuated tube surrounded by a double walled container for liquid air, insulated by wool, was illuminated with monochromatic light of constant intensity. As independently observed by Ives, the current wave-length curve at −180°C is shifted to shorter wave-lengths with respect to the curve at 20°C, the shift decreasing from about 500 A at the long wave limit 6500 A, to 80 A in the blue. These shifts are reversible and reproducible. Monochromatic heating and cooling curves run approximately parallel to the temperature axis except between −80° and −100°, where they show a sudden change. This region is where a change of crystal structure is known to take place. The shifts observed, then, seem to be due in part, at least, to the change of crystal structure. This point needs further study. Slight sudden changes of temperature produced irregular effects which are not understood; they may possibly be associated with the condensation of new vapor or with cracks in the surface.

INTRODUCTION

THE independence of photo-electric properties and the temperature of the illuminated surface has been generally regarded as well established. This conclusion rests upon a large amount of experimental data reported by several men, working under different conditions and covering various temperature ranges.

However, a study of the experimental work on photo-electricity revealed noteworthy gaps in the evidence. Practically no work at all had been done at low temperatures. Only one investigation[1] was found which reached down to the temperature of liquid air; and the alkali metals had not been studied below room temperature. Dember,[2] in 1907, investigated sodium and potassium from room temperature up through their melting points, finding no consistent changes in the photo-electric currents with increasing temperature, but he did not use monochromatic light and he made no attempt to determine long-wave limits.

For these reasons and further because the alkali metals are apt to be extreme in their behavior, the study of pure potassium was undertaken down to the temperature of liquid air. The problem of potassium at low

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[1] A. Lienhop, Ann. der Phys. **21**, 281 (1906)

[2] Dember, Ann. der Phys. **23**, 957 (1907)

temperatures had an additional point of interest due to the fact that Bidwell[3] recently discovered a sudden change in the thermo-electric power and also in the resistance of potassium at a temperature near −110°C, where a change in crystal structure occurs. Not knowing of the work of Ives[4] on this same problem, published in April, 1924, a number of the interesting effects which he reports were independently observed by the writer before Ives' paper appeared. These included the following: The absence of a well-defined long-wave limit for very pure potassium in a high vacuum; a lateral shift toward the short wave-lengths, of the curve in which photo-electric current per unit light intensity is plotted against wave-length, on cooling the cell to the temperature of liquid air; a corresponding shift in the long-wave limit; and the perfect reversibility of these phenomena.

After the appearance of Ives' paper, a detailed study of these effects was made for gradually rising temperature from −180°C up to +20°C, and indications were obtained that the shifts of the curves are due, in part at least, to the change in crystal structure.

The Cell

The photo-electric cell, made of Pyrex, had electrodes of heavy tungsten wire. The receiving electrode ended in a circle of tungsten wire, crossed by two small wires at right angles to each other. After baking the glass system thoroughly in an electric oven at 360°C, the potassium was twice distilled and then poured over into the cell with the diffusion pump running continuously.

This work of pumping and filling the cell was done at the Case Research Laboratory, Auburn, N. Y., for which thanks are due to Mr. T. W. Case, particularly for expert assistance furnished by him. The diffusion pump was of the highly-efficient, all-metal type and, with the exception of the connection to the pump, no ground glass joints or stop cocks were used in the system. It is believed that the vacuum was as high as is obtainable by such means.

Apparatus and Method

A large spectrometer with two-inch objectives was used as a monochromatic illuminator. The eye-piece with its rack and pinion were removed from the telescope and a special tube substituted into which were fitted a series of four diaphragms with parallel rectangular apertures of decreasing width as the final slit was approached. The inside of this

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[3] C. C. Bidwell, Phys. Rev. **23,** 357 (1924)

[4] H. E. Ives, Jour. Opt. Soc. Amer. and Rev. Sci. Inst. **8,** 551 (1924)

tube and both sides of all the diaphragms were covered with a jet black material having a velvet surface. Likewise the prism house was lined with black cotton flannel. No stray light could possibly enter the slit as a result of multiple reflections, the beam of light being narrowly confined to the axis of the telescope. A 60-degree flint glass prism was used, having faces three inches square.

Several sources of radiation were tried. The one finally adopted and used throughout this work was a 600-watt, 20-ampere, gas-filled lamp with a V-shaped, helical filament. The current was maintained at a remarkably constant value by means of an auxiliary storage battery, connected in parallel with the lamp and an adjustable low resistance. A low-range ammeter in series with this auxiliary battery served as a highly-sensitive control for the current through the lamp. The main rheostat, in series with the lamp, was water cooled.

The energy of the light was measured by means of a Coblentz thermopile and a Leeds and Northrup high-sensitivity galvanometer. The thermopile was mounted upon the slit in front of the photo-electric cell so that it could be moved into position for checking the calibration at will. The scale deflections for wave-lengths near the long-wave limit were as large as six or seven centimeters, decreasing to a few millimeters for λ 4359. The energy readings were highly satisfactory. Being entirely free from disturbing effects, even the smallest deflections could be repeated to one per cent. Throughout the work, slit widths of one-hundredth of an inch were used.

The photo-electric currents were measured with a Dolezalek electrometer, having a sensitivity of 2,800 mm per volt. All currents reported are saturation values. The potassium electrode was maintained at a negative potential of 120 volts.

The arrangement for temperature control of the cell is indicated in Fig. 1. The cell was supported by brass brackets within a double-walled copper box, $5\frac{1}{2}$ inches square on the inside and 6 inches square on the outside. By means of a pressure siphon, the liquid air was pumped into the air-tight cavity between the inner and outer walls of the box. It was introduced through a glass tube at the top of one end and the vapor escaped through a small glass tube at the top of the opposite end. The copper box containing the cell was mounted in the center of a wooden box twelve inches square, so that a layer of pure wool three inches thick and considerably compressed, surrounded the copper container on all sides. The beam of light, which came to a focus at the slit and thermopile, diverged through a distance of about six inches and illuminated a good-sized area on the potassium surface.

In order to minimize heat conduction, the beam of light was led to the cell through a glass tube, three inches long and one inch in diameter, on each end of which was sealed a thin plate glass window. The windows were sealed on with a pasty mixture of water glass and talcum, a cement which Oldenberg[5] found would hold a vacuum even when the joint was immersed in liquid air. This tube has held a good vacuum for a period of three months during which it has been cooled repeatedly to the temperature of liquid air. Frost formation on the inner window was prevented by a small beaker of drying material. The outside window was kept clear of frost by blowing dry air upon it. Temperatures were measured with a pentane-in-glass thermometer whose bulb rested in contact with the heavy tungsten wire leading through the cell wall into the block of potassium. The heat insulation of the apparatus is indicated by the fact that two liters of liquid air would cool the cell down to −180°C and hold it for over two hours.

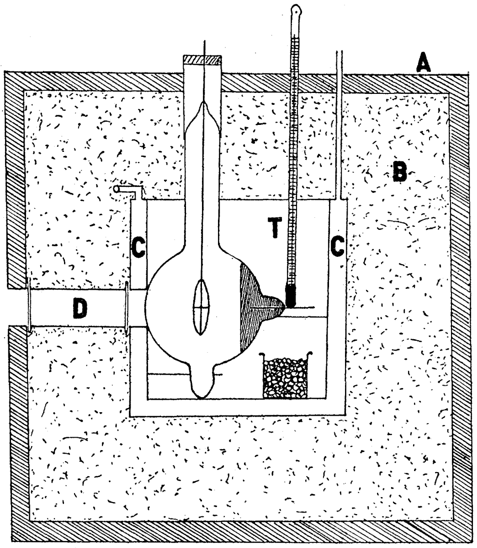

Fig. 1. The arrangement for temperature control of the cell. *A*, outer wooden box; *B*, wool packing; *C*, cavity for liquid air; *D*, evacuated tube; *T*, pentane thermometer.

Results and Conclusions

The curves in Fig. 2 are typical. They show the shift in the photoelectric currents per unit light intensity between room temperature and the temperature of liquid air. The perfect reversibility of the effect is

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[5] O. Oldenberg, Ann. der Phys. **67**, 258 (1922)

indicated by the fact that the points for two separate runs, several days apart, are plotted on each curve. These curves could be repeated at will. Fig. 3 shows these same curves in the region of the long-wave limit with the ordinates magnified twenty-seven times. The long-wave limit is not well defined, but there is no doubt that it shifts along with the curves. During the progress of the work the cell was cooled down with liquid air fourteen times. A study of the tables of data for the best runs at each temperature led to the decision that the long-wave limit was about 6500 A at 20°C and about 6000 A at −180°C. But these values are subject to an error in either direction of 100 A, or more, because of the slow approach of the curves to the wave-length axis. The corresponding values reported by Ives are 7000 A and 6200 A. That the asymptotic character of the curves in the region of the long-wave limit can be due to

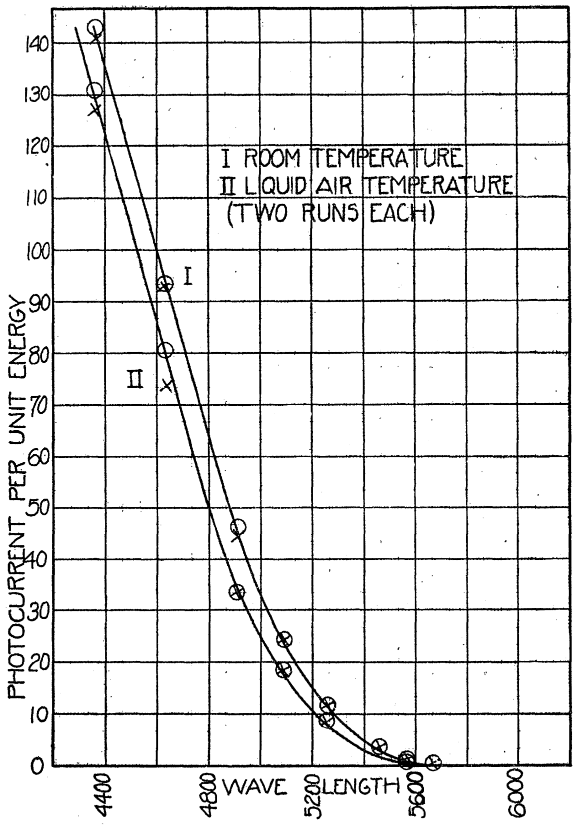

Fig. 2. Photo-current curves (I) at room temperature and (II) at liquid air temperature.

stray radiation is doubtful in view of the precautions taken in these experiments. It seems to be characteristic of pure potassium in a high vacuum. At any rate the recent work of Ives and earlier observations by Pohl and Pringsheim point also to this conclusion.

The curves in Fig. 2 do not indicate a selective effect. As a matter of fact, preliminary observations with shorter wave-lengths gave evidence of a maximum value at about 4200 A. In this region, however, the absorption of the glass prism was so great that the thermopile gave a galvanometer deflection of less than 2 millimeters, making the data too uncertain to warrant conclusions with regard to the temperature effect.

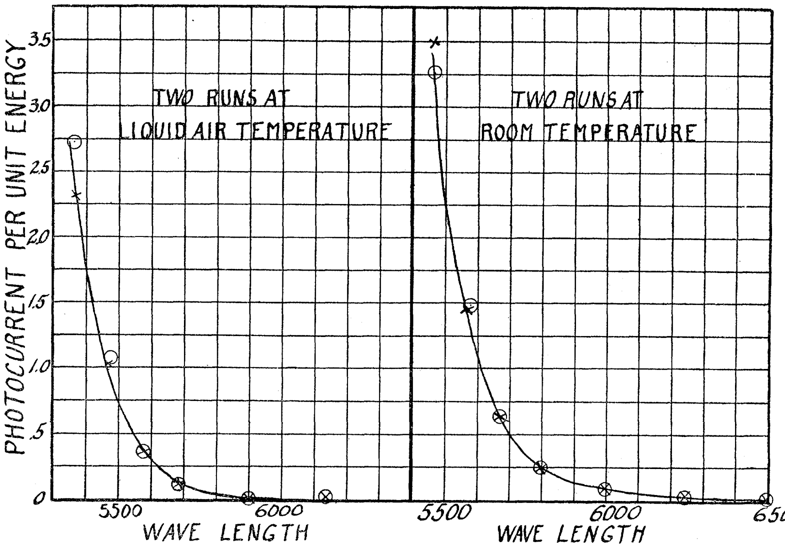

Fig. 3. Curves showing long wave limit at room temperature and at liquid air temperature.

The arrangement for temperature control of the cell was designed with the idea of holding the temperature indefinitely at any point, so that the photo-electric response could be traced in detail from −180°C to 20°C. Indeed, the temperature could be easily held constant to one-half a degree by pumping in a small quantity of liquid air whenever the thermometer indicated a slight creeping up of the temperature. After many attempts, however, this method of taking readings had to be given up because the results were inconsistent. The *sudden chilling* of the metal affected the photo-electric currents and, in general, gave abnormally high values. When liquid air was introduced with the cell at room temperature, the photo-currents for all wave-lengths always increased decidedly, and the response was sudden. This increase, as Ives has pointed out, was undoubtedly due to the condensation of potassium vapor and the formation of a partially new surface. However, the rate of fatigue of this newly deposited metal was not constant for different trials. It apparently depends upon the amount of liquid air which is pumped in at the start. Furthermore, the process of holding the cell at a given temperature, namely, by introducing a small quantity of liquid air at frequent intervals, raised the photo-currents above their normal values. This effect is not understood. It is possibly due to the fact that the mirror surface of the potassium was broken by check lines into a large number of small polygons. The sudden chilling of the metal and the consequent contraction would conceivably open up these cleavage lines of the surface and allow the incident light to reach down more deeply into the surface layer. It should, however, be pointed out that when the cavity of the box was filled with liquid air and kept full until equilibrium was obtained, the resulting photo-currents at −180°C were constant and repeatable.

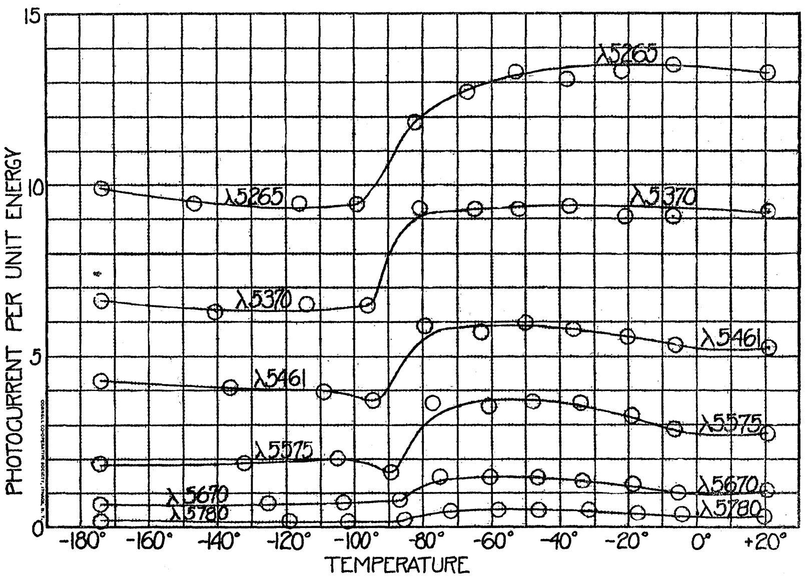

Fig. 4. Photo-current as function of temperature, for various wave-lengths.

A certain procedure gave fairly consistent results and apparently revealed one of the contributing causes of the shifts of curves like those shown in Figs. 2 and 3. This procedure was merely to cool the cell to equilibrium at −180°C, then take readings of photo-currents and corresponding temperatures while the apparatus gradually warmed up to room temperature. A set of curves so obtained is shown in Fig. 4. Temperatures were read immediately before and after the photo-electric currents, and mean values plotted in the curves. The temperature rise during the time necessary to read the electrometer deflection and check it amounted to two or three degrees at the start and gradually decreased to about one degree at $-80°C$ and to about one-half degree at $+20°C$.

An abrupt transformation point is evident in all of the curves. On each side of this point the curves are nearly parallel to the temperature axis. For shorter wave-lengths a similar though less prominent discontinuity was observed. It was not merely an accidental irregularity for it occurred repeatedly and persisted even after removing the cell from the box and melting down the potassium to form a new surface. As a change in crystal structure is known to occur in this region, correlation of the two effects is at once suggested, especially since Bidwell found a sudden change in the thermo-electric power at approximately the same temperature. However, this method of locating the discontinuity, if it is a real effect, is open to the objection that there is a temperature gradient of an unknown amount between the illuminated surface of the metal and the tungsten electrode which rested in contact with the bulb of the thermometer; moreover the cell as a whole is not in temperature equilibrium while the liquid air is boiling out of the container. The possible connection with crystal structure, therefore, requires further study, not only with potassium but also with other alkali metals.

This investigation, then, while it points definitely to the reality of the temperature effect, suggests the interesting probability that the shift of the long-wave limit is due, in part at least, to the change in crystal structure.

This experimental work was carried out at Cornell University during the winter of 1923-24, on sabbatical leave of absence from Carleton College. I am deeply indebted to Professor Merritt and other members of the Department staff for many courtesies. In particular, I wish to thank Professor F. G. Tucker, whose timely suggestions and constant interest were especially helpful.

CARLETON COLLEGE,
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