PHOTOELECTRIC PROPERTIES OF ZINC SINGLE CRYSTALS

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Abstract

An experiment is described in which the photoelectric properties of outgassed single crystals of zinc were studied. After treating the emitting surfaces of a crystal with ultraviolet light and thermally evaporating some of the zinc, a stable condition was reached. In this stable condition a difference in the long wave limits of the polycrystalline surface and cleft 0001 face of approximately 260A was observed. The results are discussed with regard to possible sources of contamination and the presence of occluded gas layers.

THERE have been only a few attempts to study the photoelectric characteristics of single crystals. Of these, only that of Linder[1] merits serious consideration. He investigated the photoelectric emission from an uncleft single crystal rod of zinc. By exposing the crystal to the total radiation of a mercury arc with various orientations of the hexagonal axis with respect to the exciting light beam, he found a maximum photoelectric current with the light beam parallel to the hexagonal axis, i.e., normal to the basal (0001) plane. He further showed that the optical reflecting power of the crystal surface was sensibly uniform and hence that the observed variations in emission were due to a real dependence of the photoelectric properties upon crystal orientation. However, he did not determine the long wave limits corresponding to the various emission values, and his vacuum conditions were not of the best.

Recent photoelectric experiments have demonstrated that, with high melting point metals, reproducible results and stable characteristics can best be obtained by subjecting the metal to an extended and vigorous heat treatment under very good vacuum conditions. It is seen immediately that such a program, in the case of a single crystal of a low melting-point metal such as zinc, is possible only in a very limited sense. Furthermore, single crystals must be handled with extreme care to prevent mechanical distortion, and their growth in an outgassed state introduces difficulties not encountered in the study of polycrystalline metals. The immediate purpose of this work, then, was to outgas a crystal of zinc as thoroughly as the above limitations permit and to study its photoelectric properties by means of monochromatic light under good vacuum conditions. However, the experiment was, in a sense, more of the nature of a study of the possibilities of photoelectric work with low melting-point crystals.

[1] Linder, Phys. Rev. **30**, 349 (1927).

Growth of the Crystals

Whereas Linder used crystals made in air by the Bridgman[2] method, for this experiment a modification of the Bridgman method, previously described,[3] was developed whereby the crystals were thoroughly outgassed and grown in good vacuum. The outgassed crystals could then remain in the evacuated and sealed-off Pyrex molds until such time as they were needed.

Photoelectric Apparatus

The photoelectric tube (see Fig. 1) was of Pyrex and was connected to the vacuum system by means of a large ground joint J used with a slight amount of sealing wax at p extending down into the joint in a very thin film for only about 1 cm. This method of sealing should decrease the rate of diffusion of wax vapor very considerably. The presence of this joint was not desirable

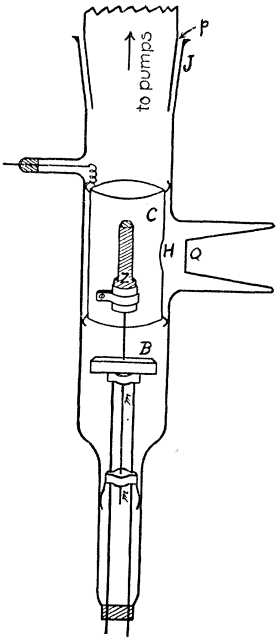

Fig. 1. Photoelectric tube.

but its use was quite necessary in order to permit transfer of the crystal from the evacuated mold to the tube with only a short exposure to the air. Light from the monochromator entered through the conically reentrant quartz window Q, through a hole H in the nickel collecting cylinder C which could be closed with a magnetic shutter, and thence was focussed upon the face of the zinc crystal z. The crystal was lightly clamped at its lower end and could be rotated about a vertical axis in the metal bearings E by means of a magnet operating on the soft iron bar B.

[2] Bridgman, Proc. Am. Acad. Arts and Sciences, **60**, 305 (1925).
[3] Dillon, Rev. Sci. Inst. **1**, 36 (1930).

The vacuum system was of Pyrex and consisted of a liquid air trap, a mercury diffusion pump backed by a Hyvac oil pump, and a McLeod gauge. The pumps were kept in operation continuously throughout the entire experiment. During this time the pressures certainly never rose above 10^{-7} mm of mercury and were considerably lower in the major part of the work.

The photoelectric currents were measured by a Compton electrometer, the quadrants of which were shunted across a high resistance of 5×10^{10} ohms. The high resistance was made by dissolving cupric oxide in soft glass and was found to be very steady after its initial fluctuation, which occupied about a week, had ceased. The electrometer and the necessary switches were inclosed in a metal shielding box through which a current of air, dried by passage through calcium chloride and a liquid air trap, could be blown. With this drying arrangement, it was possible to use the electrometer at sensitivities of 1000 to 10,000 mm per volt on the most humid summer days.

The optical system consisted of a Cooper-Hewitt quartz mercury arc operated with 80 volts across the arc, a Bausch and Lomb single monochromator, and auxiliary quartz lenses. The monochromator was carefully calibrated and studied with the purpose of learning what slit widths could be safely used. Fortunately, the long wave limit of the zinc specimens was found to lie in the region 3200A to 3700A where the mercury lines are widely spaced so that slits of width 0.3 mm which were used gave the necessary purity. Both the photoelectric current and the current from the pile were found to fall practically to zero at monochromator settings between the mercury lines 3650A, 3341A, and 3132A. This eliminated the possibility of any appreciable influence of stray light upon the long wave limit determinations.

The intensity of the light incident on the crystal was measured by a 13-junction Pt-Te vacuum thermopile connected to a Kipp Zc galvanometer. The pile was mounted directly before the exit slit of the monochromator and could be moved in and out of the light path to permit all of the light to fall either upon the crystal or upon the pile elements. The construction of the monochromator was such that the pile elements could be no closer than 12 mm to the exit slit. Hence, the receiver was large (13mm$\times$3mm) so as to intercept all of the light from the divergent cone. The variable magnetic shunt of the galvanometer was adjusted so that the critical damping resistance was equal to the resistance of the pile (44 ohms). Vacuum was maintained in the pile by means of a Hyvac oil pump giving a pressure of 10^{-3} mm of mercury.

Procedure

Before inserting the crystal for observation, the photoelectric tube, completely assembled except that the crystal was absent, was evacuated to "sticking" as indicated by the McLeod gauge which was capable of indicating pressures as low as 2×10^{-7} mm of mercury. The tube was then baked at a temperature of 400°C until the gauge indicated that the pressure was as low as before starting the furnace. The furnace was then removed and air admitted to the system. A crystal was next removed from its evacuated mold and cleft at liquid air temperature to minimize distortion. Zinc cleaves readily only

along the basal plane, which was usually nearly parallel to the axis of the cylindrical mold. Hence, only one crystal plane was available for observation. However, by taking x-ray powder spectrograms[4] it was found that a filed surface is essentially polycrystalline. Thus in addition to cleaving along the basal plane, another face parallel to it was filed at liquid air temperature so that the photoelectric properties of the basal plane could be compared with those of the polycrystalline surface. Immediately after cleaving and filing, the crystal was clamped into place in the photoelectric tube which was sealed on the system and evacuated. The total time during which the crystal was exposed to the air was usually about 20 minutes and never exceeded 40 minutes. Thus it is reasonable to suppose that very little gas would return to the volume of the metal, and that only a surface layer would result.

In an effort to remove this surface layer of gas, two methods of treatment were applied. Winch[5] and others[6] have found that a metal surface can be at least partially outgassed by irradiation in vacuum with intense ultraviolet light. This method which may be termed "ultraviolet outgassing," when applied to the zinc surfaces, produced very marked changes as will be shown later. In addition, the crystals were baked at temperatures at which a large amount of the zinc evaporated.

Results

Six zinc crystals were studied in the course of this experiment. Inasmuch, however, as none of the results from any of the crystals were discordant, only crystal #5, which was subjected to a greater variety of conditions than any of the others, will be discussed in detail. When observations on crystal #5 were first taken soon after its insertion in the tube, the photocurrents from both the polycrystal face and the cleft 0001 (Bravais indices) plane were found to decrease rapidly with time of exposure to the exciting light. This state in which the photocurrents decreased with time of exposure was never encountered with any of the other crystals. Apparently, upon treatment with the full arc, this was soon supplanted by the usual state where the photocurrents increased with time of exposure, for it was never again observed. Since, in this initial state, no dependable readings could be taken, an "ultraviolet outgassing process" was immediately begun. This was accomplished by directing the total radiation of a Cooper-Hewitt quartz mercury arc upon the face of the crystal. This process was continued for roughly 150 hours, during which time the photocurrents from both the polycrystal surface and the 0001 face increased very rapidly at first, and then more slowly approached limiting values above which further treatment caused no change. At this stage of the experiment "fatigue tests" were made at daily intervals for a week. It was found impossible to change the amount or rate of fatigue (diminution of photocurrent with time with light off) by further treatment with ultraviolet. After cutting off the light of the full arc, the photocurrents decreased quite

[4] Hanawalt, Ph. D. Thesis, University of Wisconsin (1929).
[5] Winch, Phys. Rev. **36,** 601 (1930), **38,** 321 (1931).
[6] Millikan, Phys. Rev. **29,** 85 (1909).

rapidly at first and then more slowly approached a constant and reproducible "fatigued" value (60 percent of initial value) which was attained in about eight hours. A relatively short time of exposure, 20 minutes, was required to restore the fatigued surface to the condition where the photocurrent had the maximum value. Long wave limit determinations were made for both the 0001 and the polycrystal face in the two states, the fatigued state (see Fig. 2, curves Ia and Ib) and the unstable state (see curves IIa and IIb). The long wave limit was found to be approximately the same for the two faces in both states and was roughly equal to 3400A.

After it was found that no further change in the characteristics could be produced by exposure to ultraviolet, the tube was enclosed in a furnace whose temperature was raised very slowly so as to maintain continuously a "sticking vacuum." After the furnace had been maintained for 36 hours at 260°C,

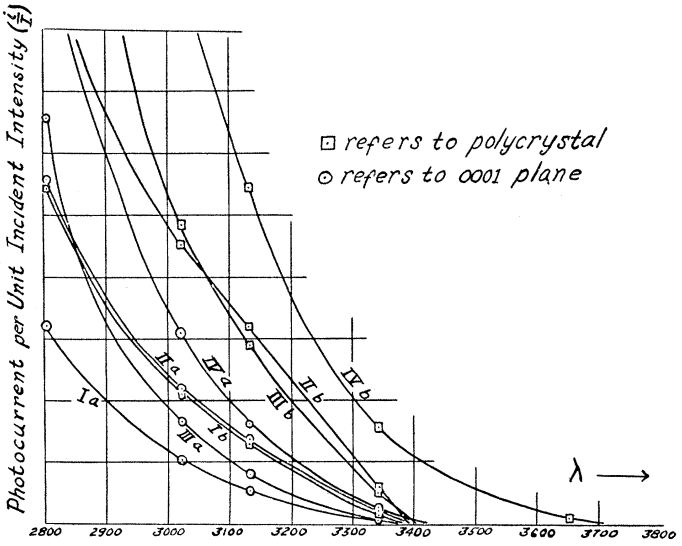

Fig. 2. Curves for crystal No. 5.

at which temperature a large amount of zinc was evaporated from the crystal, the furnace was removed and a long wave limit test was made. This revealed that the photocurrents from both faces had increased to a steady value as indicated by curves IIIa and IIIb, but the long wave limit remained at its former value for both faces. It was now found, and this is the most striking result, that exposure to ultraviolet light after distillation from the surface not only increased the photo-currents still farther but resulted in changes in λ_0 to the values 3460A for the 0001 face and 3720A for the polycrystal as given by curves IVa and IVb. Fatigue tests taken at this point showed less than 2 per cent fatigue in a period of 4 hours for both faces. Fig. 3 gives curves IVa and IVb plotted logarithmically in an attempt to determine λ_0 more accurately.

It was suggested by Dr. Roebuck that possibly the difference between the 0001 and polycrystalline faces which appeared after distillation and ultra-

violet treatment was due to the contamination of the polycrystal face by the clean file used in producing it. To check this, a third face was prepared on crystal #6 by scraping with tungsten carbide, this being the hardest substance available which could be cleaned with acids. The scraped and filed surfaces

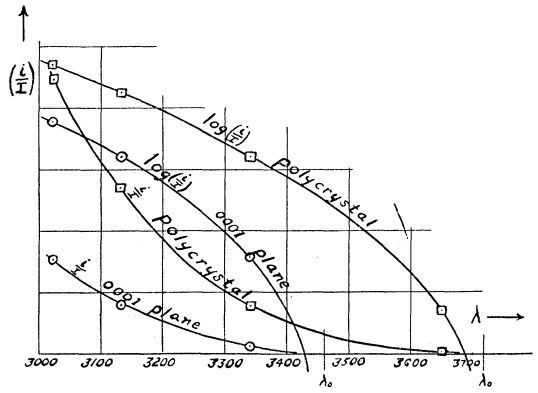

Fig. 3. Final stable state for crystal No. 5.

behaved in exactly the same way so that contamination from this source appears to be ruled out. In this case the final values of λ_0 were 3465A for the 0001 face and 3730A for the polycrystal surface.

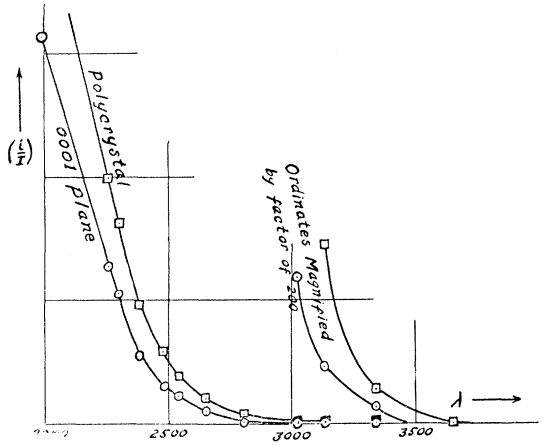

Fig. 4. Final stable state for crystal No. 6.

In addition to this direct study of λ_0, a number of curves were obtained over the entire range of wave-lengths (2000A–3800A) permitted by the monochromator. All of these curves were of the same general form as that of Fig. 4 and failed to show any kind of "selective" maximum.

Conclusions

At present no reliable value of λ_0 for zinc is to be found in the literature. Küstner,[7] Welch,[8] Lukirsky and Prilezaev,[9] Hamer,[10] Hennings,[11] and Rich-

ardson and Compton[12] have made determinations of λ_0 for zinc, but in no case were their experimental conditions good enough to warrant attaching much significance to the results. It is true that, in some cases[7, 8, 11, 12], the surface of the zinc was scraped or filed in fairly good vacuum, but no attempt was made to remove the gas from the volume of the metal. Hughes[13] determined λ_0 for zinc which had been freshly distilled in vacuum. However, he stated the pressure in the tube to be of the order of 5×10^{-4} mm, so, although his work seems superior to that of the others, it cannot be taken too seriously in the light of present day vacuum and outgassing requirements. The present experiment is, then, the first attempt to apply modern photoelectric technique to zinc in either single crystalline or polycrystalline form.

There is a possibility that the action of the intense ultraviolet light was not to outgas the metal surfaces but rather to accelerate a chemical reaction of the zinc with the residual gases in the system. The chemical compound thus formed might explain, then, the observed difference in long wave limits. However, it was observed in the case of crystal #3, which had never been exposed to intense ultraviolet light, that heating by radiation from a filament inserted in a side tube caused a large increase in the photocurrents. Crystal #5, after the first treatment with ultraviolet light, was exposed to the radiation of the filament at the same temperature for the same length of time and no measurable change in the photocurrents occurred. This would seem to indicate that the ultraviolet light actually removed gas from the surfaces.

The outgassing treatment in this experiment was, for reasons already given, less vigorous than that usually used for high melting-point polycrystals. Thus it may be argued that a really clean surface was never attained, but instead some stable intermediate state such as might exist with a monomolecular gas layer on the surface. At present, it seems impossible to refute this argument completely, although in the final state, the rate of fatigue was very small, which condition is commonly assumed to characterize a perfectly clean surface. However, the large difference in the long wave limits ($\Delta\lambda_0=$ 260A) cannot be attributed entirely to the effect of ordinary gas layers. Of course, it is possible that the gas layers may be present on the crystal face in the form of a "gas lattice" which might have a different effect on the photoelectric properties than the layer formed on the polycrystalline surface. It seems, therefore, impossible to conclude whether the observed difference in the long wave limits for the 0001 plane and the polycrystal is due to a real dependence of the photoelectric work function upon crystal geometry or to the effect of a possible absorbed gas lattice which itself would depend on crystal structure. It is hoped that this experiment which, with its several

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[7] Küstner, Ann. d. Physik **46,** 893 (1915).
[8] Welch, Phys. Rev. **32,** 657 (1928).
[9] Lukirsky and Prilezaev, Zeits. f. Physik **49,** 236 (1928).
[10] Hamer, Jour. Opt. Soc. Am. **9,** 251 (1924).
[11] Hennings, Phys. Rev. **4,** 228 (1914).
[12] Richardson and Compton, Phil. Mag. **24,** 575 (1912).
[13] Hughes, Phil. Trans. Roy. Soc. London **212,** 205 (1912).

limitations, nevertheless was performed as carefully as present photoelectric methods permit, will lead to further study which will give more definite information concerning the photoelectric properties of single crystals.

Quantitative comparison of these results with those of Linder seems a hopeless task, for his photoelectric emmission came from the facets or surfaces of the negative crystals, so that a given orientation of the crystal axis with respect to the exciting light beam in his experiment gives no assurance that the corresponding emission was due to the plane normal to the light beam.

R. H. Fowler[14] has developed a theory for the effect of temperature on the photoelectric sensitivity of a clean metal near the threshold. He gives a graphical method enabling the whole of the observed curves near the threshold for all temperatures to be used in determining the threshold itself thus avoiding an arbitrary extrapolation to zero current. Curves IVa and IVb were plotted in the reduced variables required by Fowler's scheme and an attempt was made to fit them to his theoretical curve. No satisfactory "fit" could be obtained and thus no conclusions could be drawn as to the true thresholds for the polycrystal and 0001 surfaces or zinc. It may be pointed out, that due to lack of data on the reflecting power of the 0001 plane of zinc, in the region 3000A–3800A, the curves IVa and IVb were not corrected for reflected light. However, the only available data on the reflecting power R of polycrystalline zinc[15] show a very slow variation of R with wave-length in this range. Hence, the lack of correlation with the theory must be due, for the most part, to the presence of some factor which is a function of frequency and which plays a more important role for zinc than for the several metals discussed in Fowler's paper.

I wish to express my appreciation of the many helpful suggestions given me by Professor C. E. Mendenhall, under whose direction this work was done, and of the assistance of Mr. C. F. DeVoe in the later stages of the experiment.

[14] Fowler, Phys. Rev., **38,** 45 (1931).
[15] Meier, Ann. d. Physik **31,** 1017 (1910).