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Measurements on Contact Potential Difference Between Different Faces of Copper Single Crystals

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Measurements on the contact potential difference between the (111) and (100) faces of copper single crystals, at different stages of outgassing, were made by the Kelvin null method. Two sets of observations with different experimental tubes show that the (111) face assumes a positive potential with respect to the (100) face. This value increased rapidly from near zero to about 0.4 volt during the first few hours of outgassing at a dull red heat and then more slowly to a limiting value of 0.446±0.002 volt at 20 hours in the first series and 0.463±0.002 volt at 70 hours in the second series of measurements. Further heating at temperatures which exposed other faces by evaporation caused the value, in the first series, to decrease to 0.384 volt after 100 hours of outgassing, and in the second series, after 275 hours, it decreased to 0.378 volt. This value, 0.378 volt, remained constant for the next 770 hours of outgassing. This difference between the results of the two series of measurements is due to different rates of outgassing. Observations were taken at pressures of about 5×10^{-8} mm Hg as measured on an ionization gauge. The outgassing was more than that required to reduce the surface gas layer to such thickness that it possesses a definite crystal structure related to that of the underlying copper, as shown by Farnsworth. Thus the above results should be characteristic of the single crystals contaminated with undesired crystal facets and probably covered with small traces of gas of crystalline structure, both of which reduce the effective value. These results definitely indicate that the contact potential difference between the (111) and the (100) faces of uncontaminated copper single crystals must be greater than the final value obtained here and most probably greater than the maximum value of 0.463 volt.

I. INTRODUCTION

THE experiments of Dowling,[1] Linder,[2] Dillon,[3] and Nitzsche[4] indicate that the intrinsic surface potentials of such metals as bismuth and zinc depend on the crystal orientation at the surface. Most of the evidence is only qualitative and in no case have crystals been used which could be outgassed at red heat in a high vacuum. Further, the metals used have a hexagonal space lattice so that it is uncertain whether more symmetrical crystals of face-centered cubic lattice, such as copper, would show an asymmetry. The purpose of the present experiment was to determine by the Kelvin null method a possible contact potential difference (c.p.d.) between the (111) face and the (100) face of copper single crystals at different stages of outgassing.

II. PREPARATION OF SINGLE CRYSTALS

The specimens were obtained from a large crystal[5] grown in an atmosphere of hydrogen by the slow progressive cooling method. The geometric faces of the two pieces of crystal, each of about 3 cm^2 test surface area, were made parallel to the desired crystal planes by a method similar to that described by Farnsworth.[6] A scratch-free surface was obtained by grinding on plate glass with very fine wet emery powder. The sides and back of each crystal were etched in ammonium persulphate solution and washed in distilled water before it was placed in its mounting.

The final test surface of the mounted (111) crystal was obtained by electrolytic etching (30 milliamperes at 0.8 volt) in copper sulphate solution. This produced a smooth surface which gave reflections over all the test surface from the desired crystal planes and gave very few

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[1] P. H. Dowling, Phys. Rev. **31**, 244 (1928).

[2] E. G. Linder, Phys. Rev. **30**, 649 (1927).

[3] J. H. Dillon, Phys. Rev. **38**, 408 (1931).

[4] A. Nitzsche, Ann. d. Physik **14**, 463 (1932).

[5] For purity of copper see, H. E. Farnsworth, Phys. Rev. **40**, 690 (1932).

[6] H. E. Farnsworth, Phys. Rev. **34**, 683 (1929).

from other crystal facets. The final etching of the test surface of the mounted (100) crystal was done in nitric acid (65 percent solution by volume), which produced a smooth surface with but very few undesired reflections, and those only from the sides of deep pits. After the final etching and washing in distilled water, the crystals themselves were not touched again.

III. Apparatus and Procedure

Two series of measurements were conducted in different experimental tubes to eliminate possible effects due to the geometry of the arrangement. A T-shaped Pyrex tube of 4 cm diameter was used for the first, and a straight Pyrex tube of 5.5 cm diameter was used for the second series of measurements. Only the second tube (Fig. 1) and set-up with the essential changes will be described here.

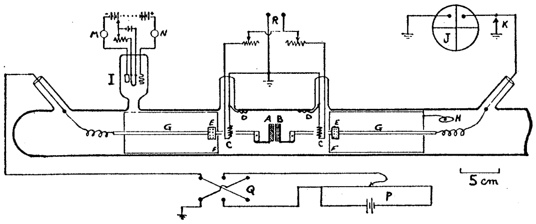

FIG. 1. Second experimental tube. *A*, (111) crystal; *B*, (100) crystal; *C*, bombarding filaments; *D*, connection to film; *E*, soft iron bar; *F*, frame of sliding mechanism; *G*, bearing tubes; *H*, ground connection; *I*, ionization gauge; *J*, quadrant electrometer; *P*, potentiometer.

This tube contained a single metal frame, which supported the sliding mechanism of each crystal. This mechanism consisted of two Pyrex tubes of small diameter held parallel to each other by a bar of soft iron and a molybdenum strip to which was attached the crystal mounting. The motion of either crystal, necessary for a measurement by the Kelvin null method, was provided by an external magnet acting on the iron bar. The initial separation of the crystals, about 0.5 mm, was determined by stops adjusted before assembly.

The electrostatic shielding was obtained by evaporating a molybdenum film on the inside of the tube and coating the outside with "aquadag" except for a portion between the filaments which was covered with a fine nickel gauze,—all of which, together with the filaments and frame of the sliding mechanism, were grounded. Shielded symmetrical leads from the crystals and shielded leads from the potentiometer and electrometer were brought to a metal switch box, which facilitated quick changes of connections by means of spring connectors, and also kept shielding conditions stable.

In the second tube the distance of the crystals from the shielding was increased considerably and the sliding mechanisms and supporting frame were constructed more ruggedly. The pressure during outgassing was measured more accurately by attaching the ionization gauge closer to the point where the crystals were heated. For the first experimental tube, the vacuum system consisted of two mercury diffusion pumps, with a liquid air trap in the lead to the experimental tube and one in the lead to the oil fore pump. An additional trap was inserted in the lead to the second experimental tube. No change in the c.p.d. was observed when carbon dioxide snow in acetone was used as the cooling agent instead of liquid air.

First series of measurements

The system was evacuated and the tube baked for 50 hours at a temperature over 400°C. A value of the c.p.d. between the crystals was read directly on the potentiometer when a motion of the crystal connected to the potentiometer caused no deflection of the electrometer. This value was then checked by reversing all connections. With an electrometer sensitivity of about 3000 mm per volt, the accuracy of a measurement was such that 0.002 volt difference from the measured value caused a noticeable electrometer deflection.

The crystals could be outgassed simultaneously by electron bombardment—the backs being protected by thin molybdenum covers. The outgassing temperature was about 900°C, based on estimates of the color of the crystals. The measurements were interrupted at the end of 21 and 60 hours of outgassing, at which points the shielding was removed and the tube baked for periods of 20 and 40 hours, respectively. The pressure, as measured on an ionization gauge, was less than 10^{-6} mm Hg during the last periods of outgassing, and less than 8×10^{-7}

mm Hg when measurements on the c.p.d. were made.

Second series of measurements

The crystals used in the first series of measurements were resurfaced by grinding on plate glass, etched in the same manner and placed in the same mountings that were previously used. The second tube, with the improvements described above, was evacuated and baked for 40 hours at a temperature over 450°C. The tube was baked for 35 hours after the crystals had been simultaneously outgassed for 150 hours. The outgassing temperature for the first 350 hours was about 650°C, and the subsequent outgassing was done at about 800°C. The pressure gradually decreased from about 3×10^{-6} mm Hg during the initial stages of outgassing, to about 10^{-7} mm Hg during the final heating periods. Throughout this series of measurements, at the time when the measurements on the c.p.d. were made, the pressure was less than 10^{-7} mm Hg and near the conclusion of the measurements it was less than 5×10^{-8} mm Hg.

IV. PRELIMINARY INVESTIGATION

A preliminary investigation was made to see if it is possible to obtain zero c.p.d. between polycrystalline plates of copper.[7] During alternate outgassing the c.p.d. fluctuated between ±0.1 volt. After a total outgassing of 25 hours the final c.p.d. was 0.01 volt which may be attributed either to incomplete outgassing or to differences in crystal orientation.

V. DISCUSSION AND ANALYSIS OF RESULTS

A measurement of the c.p.d. between the two crystals, immediately after each baking of the tube and before heating by bombardment, gave a value which was near zero, indicating that the baking process allowed the liberated gases to condense on the crystals and thus produce surfaces which were nearly alike. As these contaminations were gradually removed by the outgassing, the value increased rapidly, the (111) face becoming more electropositive with respect to the (100) face. Subsequent heating caused the c.p.d. to pass through a roughly defined maximum of 0.446 volt for the first series of measurements and 0.463 volt for the second series, and to approach a steady value of 0.384 volt and 0.378 volt for the first and second series of measurements, respectively.

In view of the positive results, it follows that the presence of other exposed crystal faces should affect the measured value. Figs. 2 and 3 are consistent with the view that the initial increase in the c.p.d. is due to outgassing of the crystals, and that the growth of undesired crystal facets, caused by evaporation, decreases this value. It appears that on continuing the heating a state is reached where changes due to these two effects are of the same order of magnitude, and the measured c.p.d. is a maximum. Early in the second series of measurements the outgassing temperature was much lower than at the corresponding time in the first series. Probably fewer undesired crystal facets appeared at the lower temperature, and as a result the maximum c.p.d. is greater in the second series of measurements.

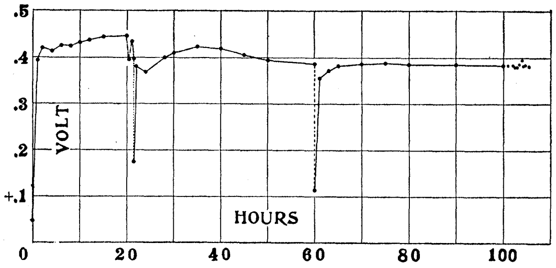

FIG. 2. Contact potential of (111) face with respect to (100) face as a function of outgassing time. (First series of measurements.)

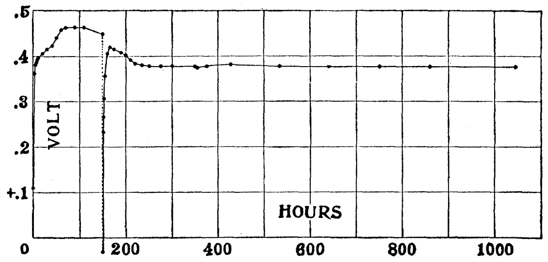

FIG. 3. Contact potential of (111) face with respect to (100) face as a function of outgassing time. (Second series of measurements.)

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[7] This copper was obtained from the research laboratory of the General Electric Company.

Further heating undoubtedly increased the number of undesired crystal facets, thereby causing the measured value to decrease. It seems reasonable to suppose that beyond a certain point the addition of a number of new facets would have a comparatively minor influence. Then the c.p.d. should be reasonably constant.

After the first 20 hours of simultaneous outgassing, the crystals were outgassed one at a time (see Fig. 2). The resulting relatively large change in the c.p.d. indicates that the crystals were still not well outgassed. At the end of 100 hours of simultaneous outgassing, only a small change in the value was observed when the crystals were heated one at a time. It is certain that the crystals were still not completely outgassed after this heat treatment, but it seems evident that a state of equilibrium was very nearly attained for the particular outgassing temperature and pressure.

In the second series of measurements, Fig. 3, the fluctuation in the value at 350 hours is probably due to an observed increase in pressure during outgassing. No change in the value occurred when the crystals were heated one at a time at 750 hours. The remarkable steadiness of the value at 0.378 volt, from 400 to 1045 hours of outgassing is attributed to the small influence of the various factors which tend to change the c.p.d. or to an equilibrium of these factors. Following this outgassing treatment, the crystals were accidentally and later deliberately heated at pressures of about 2×10^{-6} mm Hg. The resulting decrease of the c.p.d. from 0.378 to 0.28 volt is probably due to the formation of denser gas layers on the surface of the crystals. Subsequent outgassing at pressures of about 3×10^{-7} mm Hg caused the value to become steady at about 0.35 volt. No appreciable change in the c.p.d. was noted when the crystals were allowed to stand at low pressures and room temperatures for days at a time. The value decreased slightly when air at a pressure of about 10^{-5} mm Hg was let into the system.

In experiments on the diffraction of electrons from the (100) face of a copper single crystal, Farnsworth[8] found a number of beams indicating a surface layer of gas of simple-cubic, single-spaced structure having the same lattice constant as copper. When the gas layer became thin after sufficient outgassing, it changed over to a double-spaced, face-centered structure. In view of these results, the present outgassing has been more than sufficient to reduce the surface gas layers to a double-spaced, face-centered structure. It seems probable that, in the interval of 700 to 1045 hours of outgassing, the surface gas layers had been reduced to an even less dense structure.

The exact value of the c.p.d. at the end of the measurements is not of as much significance as the fact that it is still large. The measured value between the outgassed crystals was greater than 0.37 volt, at pressures of the order of 10^{-7} mm Hg throughout most of the experiment, and also at pressures less than 5×10^{-8} mm Hg. Since near the end the pressure during heating differed but slightly from that measured when the crystals were cold, it is concluded that the crystals were well outgassed and that further heating would not appreciably alter the c.p.d., except to decrease it by exposing undesired crystal facets. Thus the final value should be characteristic of the single crystals contaminated with undesired crystal facets and probably covered with small traces of gas of crystalline structure, both of which reduce the effective value. A more detailed interpretation is given elsewhere.[9]

The results definitely indicate that the contact potential difference between the (111) face and the (100) face of uncontaminated copper single crystals must be greater than the final value obtained here and most probably greater than the maximum value of 0.463 volt. This is much greater than was anticipated for a symmetrical cubic crystal and indicates the desirability of extending the investigation to other crystals.

The author wishes to express his most sincere appreciation of the help received from Professor H. E. Farnsworth, who suggested the problem and made invaluable suggestions throughout the course of the development. The major portion of this work was done while the author was a recipient of a Brown University Fellowship.

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[8] H. E. Farnsworth, Phys. Rev. **40**, 684 (1932).

[9] H. E. Farnsworth and B. A. Rose, Proc. Nat. Acad. Sci. **19**, 777 (1933).