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WORK-FUNCTION DEPRESSION AND SURFACE IONIZATION FOR PLANAR (100) TUNGSTEN EXPOSED TO CESIUM

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MIT Physical Electronics Conf.-Boston, Mass.
March 28, 1966.

UCRL-16805

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AEC Contract No. W-7405-eng-48

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Abstract

Currents due to electron and ion emission were measured in a cesium diode with a planar monocrystalline (100) tungsten emitter as a function of applied voltage, emitter temperature (850 to 1450°K) and cesium reservoir temperature (0 to 100°C). The work-function depression due to cesium adsorption was evaluated from field-free electron emission data by means of the Richardson equation and from field-free ion emission data by means of the Saha-Langmuir equation. Results from the two methods agree within 2% for emitter temperatures below the threshold temperature for ionization. The threshold temperature occurs at an emitter-to-cesium reservoir temperature ratio of 3.5. Work function depressions as great as 2.9 eV, corresponding to an inferred cesium coverage of 0.6 - 0.7 of a monolayer, were obtained. The variation of work function with emitter-to-cesium-reservoir temperature ratio agrees reasonably well with theory.

Introduction

The presence of adsorbed cesium on a metal surface results in an effective surface work function which is less than that for a bare surface. The concentration of cesium adsorbed on a metal surface exposed to cesium vapor is determined by the equilibrium between the rate of evaporation of the adsorbed cesium and the flux of cesium incident on the surface. A theoretical description of these phenomena involves, in part, a knowledge

* This work was supported by the Inorganic Materials Research Division of the Lawrence Radiation Laboratory and by the Space Sciences Laboratory of the University of California

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of the bare work function of the emitter surface and ion and neutral-atom desorption energies. Our recent measurements[1] of these properties for planar monocrystalline tungsten surfaces are described elsewhere[2] in these proceedings. We present here results of our experimental investigations of work function depression and ion emission for (100) planar tungsten as a function of emitter temperature and cesium-reservoir temperature. Effective work functions were evaluated from field-free electron emission data by means of the Richardson equation and from field-free cesium-ion emission data by means of the Saha-Langmuir equation. These results are compared with theoretical predictions and also with earlier experimental data for polycrystalline tungsten.

Experimental Procedure

Electron and cesium-ion emission measurements were made using the diode described in our previous paper[2]. A complete current-voltage curve within the range -300 to +300 V was obtained point by point for each chosen emitter and cesium-reservoir temperatures. The emitter temperature was normally held fixed while the cesium-reservoir temperature was varied through all or part of its range. The temperature range of the emitter at which we obtained useful emission data in cesium was 850 to 1450°K and that of the cesium reservoir was 0 to 100°C. The cesium-reservoir temperature was controlled to within $\frac{1}{4}$°C and was accurately measured with direct-contact thermocouples. All other parts of the diode were maintained at temperatures well above the reservoir temperature. The interelectrode spacing was maintained in the range 0.010 to 0.020 in., as measured by a cathetometer. These parameters insured a condition of collisionless plasma in the interelectrode space.

Electron-Emission Measurements

The electron-current distribution (i.e., the Boltzmann line) in the retarding-potential region was readily measurable whenever the emitter work function was low enough that the ion emission from the emitter was negligible compared to the saturation electron current. The slope of the Boltzmann lines yielded electron temperatures 50 to 100°C greater than the measured emitter temperature. Under these conditions, and in the absence of space-charge limitations, the knee (contact potential) of the current-voltage curve was very sharply defined (within 50 mV). From these measurements the collector work function was determined and found to vary within the range 1.95 $\pm$ 0.05 eV as the collector-to-cesium-reservoir temperature ratio varied from 1.1 to 1.3.

The field-free electron emission J_{so} was determined from the intercept, at zero interelectrode potential, of Schottky plots of the observed electron current. The effective emitter work function ϕ for each combination of emitter temperature T_E and cesium-reservoir temperature T_{Cs} was determined from the Richardson equation,

$$\phi = kT_E \ \ln A - \ln \frac{J_{so}}{T_E^2} \qquad (1)$$

The value of the constant A used in this calculation was 238 ampere/cm^2 °K^2, as determined from our vacuum data[2]. Results for (100) tungsten are shown in Fig. 1. Also drawn on this figure are lines of constant negative slope representing calculated emission currents for the constant emitter work function indicated on each line.

Carabateas[3] and Rasor and Warner[4] predict that the depression $\Delta\phi$ of the emitter work function due to cesium adsorption should be a nearly unique function of the ratio T_E/T_{Cs} of emitter temperature to cesium reservoir temperature. Our (100) tungsten data are plotted versus this ratio in Fig. 2, using our measured value of the bare work function $\phi_o(100) = 4.65$ eV[2]. The upper of the two narrowly spaced lines represents data cesium-reservoir temperatures from 40 to 80°C and the lower line represents data at 100°C. This small trend with cesium temperature is consistent with the theory of Rasor and Warner. Fig. 2 was used to extrapolate the curves of Fig. 1 beyond the range of the data.

Comparison With Data of Taylor and Langmuir

Also shown in Fig. 2 is a curve determined from the data obtained by Taylor and Langmuir[5] from experiments on an initially polycrystalline tungsten wire emitter. The curves for (100) and polycrystalline tungsten shown in Fig. 2 are very nearly identical in shape but are displaced horizontally, such that at constant $\Delta\phi$

$$\frac{T_E}{T_{Cs}}(100) = \frac{T_E}{T_{Cs}}(\text{poly}) - 0.15 \qquad (2)$$

We have already seen[2] that our measurements of the bare work function ϕ_o and cesium ion and atom desorption energies ϕ_{io} and ϕ^*_{ao} for (100) tungsten are essentially identical with those of Taylor and Langmuir for polycrystalline tungsten. The displacement between these two sets of data, as shown in Figure 2, may be due to differences in the surface density σ of an adsorbed cesium monolayer and/or to differences in vibrational frequencies Q_{ao} of the adsorbed cesium, both of which affect surface coverage and degree of work-function depression.

A general relation which is applicable to the theories of Rasor and Warner[4], Carabateas and co-workers[6], and Levine and Gyftopolous[7][8] relates the work-function depression $\Delta\phi$ at a given temperature T_E and cesium coverage temperature ratio, T_E/T_{Cs}, as follows:

$$\Delta\phi(\theta,T_E) = \frac{1}{1-f(\theta)}\left\{\phi^*_{ao} - h\frac{T_E}{T_{Cs}} - kT_E\left[\ln\frac{Q_{ao}\sigma}{C} + K(\theta)\right]\right\} \qquad (3)$$

where θ is the fraction of an adsorbed monolayer on the emitter surface, h and C are temperature-independent properties of cesium, and k is the Boltzmann constant. Using the functions $f(\theta)$ and $K(\theta)$ and corresponding constants suggested from each theory, and adjusting the ratio Q_{ao}/C so that each theoretical prediction is normalized to the data of Taylor and Langmuir at $\Delta\phi = 2.0$ eV, we arrive at the comparison in Fig. 3 between theory and the Taylor-Langmuir data. Using this same adjusted ratio of Q_{ao}/C with our measured parameters[2] for (100) tungsten results in the comparison between theory and this experiment as shown in Fig. 4.

Ion-Emission Measurements

Cesium-ion currents were measured under conditions of 100% surface ionization to determine the flux of cesium vapor incident on the emitter as a function of cesium-reservoir temperature and under conditions of low fractional surface ionization to evaluate the emitter work function from the Saha-Langmuir equation. To determine the field-free saturation ion emission in the latter case, Schottky plots such as those shown in Fig. 5 were made. A typical set of ion current versus applied collector voltage for the condition of 100% surface ionization is shown in Fig. 6. The saturation current was taken to be the value of the current at the knee of each curve, where the data were quite reproducible. At lower voltages the ion currents were space-charge limited and followed the 3/2 power law of Child-Langmuir applied to cesium ions. The position of the space-charge limited region confirmed the cathetometer measurements of the interelectrode spacing within 10%. Step increases in voltages above that of the knee resulted in damped oscillations of the ion current with gradually increasing initial amplitudes and with periods on the order of a few seconds. At the greatest applied voltage indicated on each curve the oscillations began to diverge and the experiment was terminated.

The saturation ion-current densities for (100) tungsten are plotted versus the reciprocal emitter temperature for various cesium-reservoir temperatures in Fig. 7. The shaded portions represent the transition between the condition of essentially complete surface ionization and that

of decreasing fractional ionization with decreasing temperature. The effective emitter work function was determined from the data of Fig. 7 and the Saha-Langmuir equation for each observed combination of T_E and T_{Cs}. For reasons discussed later the saturation currents of Taylor and Langmuir[10], whown by the arrows in Fig. 7, were used in computing the degree of ionization. Work-function depressions obtained by this method are compared with our electron-emission results in Fig. 8. The excellent agreement between the two methods at values of T_E/T_{Cs} less than 3.5 is an indication of the uniformity of the work function over the crystal surface. The two curves depart from each other at values of T_E/T_{Cs} above 3.5 because the corresponding effective emitter work function becomes greater than the cesium ionization potential. In this region the surface coverage of cesium is greatly influenced by the polarity of the applied electric field needed to observe either the electron or ion emission from which the work functions are evaluated. At lower T_E/T_{Cs}, where degree of ionization becomes relatively small, the surface coverage is determined largely by the evaporation rate of neutral cesium, and polarity of the applied field has negligible effect.

Cesium-Vapor Flux

The average saturation ion currents at 100% surface ionization, represented by the horizontal part of the curves in Fig. 8, are plotted against the reciprocal cesium-reservoir temperature in Fig. 9. Also included are data taken on (110) tungsten in an earlier assembly of this diode, as well as the data of Taylor and Langmuir[10] for a polycrystalline wire emitter. The temperature range of the measurements for a wire emitter were recently extended to 100°C by Carney[11] in this laboratory, and the accuracy of the Taylor-Langmuir data was confirmed. The saturation currents measured in our planar geometry are a factor of about 1.5 greater than those of Taylor and Langmuir. Possible temperature inaccuracies and/or cesium impurities, which were carefully controlled, cannot account for this discrepancy. Because all data shown here were obtained for similar ranges of applied voltage, possible secondary electron emission at the collector cannot account for these observed differences in saturation currents.

It is likely that our higher saturation currents result from the geometry of our closely spaced planar electrodes, as compared with the cylindrical collector and wire emitter used by Taylor and Langmuir. In the absence of an interelectrode electric field, thermodynamic equilibrium with the cesium vapor outside the interelectrode space is established by

by cesium leaving the emitter and collector isotropically at equal rates in planar geometry but almost entirely by cesium leaving the collector in wire-cylindrical geometry. A negative bias applied to the collector to obtain saturated ion currents collimates the ions towards the collector and removes the emitter as a source of cesium to establish equilibrium with the cesium outside the interelectrode space. This has little effect upon cesium equilibrium in wire-cylindrical geometry, but the planar collector can maintain cesium equilibrium only by developing a thicker layer of adsorbed cesium and emitting cesium at much greater rate than in the field-free condition. This must necessarily increase the neutral flux incident upon the emitter and thereby increase the observed ion current. Such an increase in ion current should be observable if sufficient time is allowed for equilibrium to be reestablished after applying the collecting potential, and the possible increase is commensurate with the ratio of our ion currents in planar geometry to those of Taylor and Langmuir.

Sputtering of neutral cesium from the collector could also account for a higher observed ion current in planar geometry if data are taken in a time before the cesium in the interelectrode space has reached equilibrium with the outer environment. Sputtered cesium would contribute little to the transient neutral flux incident upon the emitter in wire-cylindrical geometry.

Ion currents for determination of work function were measured under conditions of relatively low degree of surface ionization, so that the applied collecting potential had relatively little effect upon the angular distribution of total cesium leaving the emitter surface. Therefore, for relatively low surface ionization the saturation currents of Taylor and Langmuir should represent the neutral flux incident upon the emitter and have been used here as the basis for relating our measured ion currents to the degree of surface ionization.

Threshold Temperature For 100% Surface Ionization of Cesium

The threshold temperature T_{EO} is loosely defined as that emitter temperature at which, for a given incident flux of cesium, a transition occurs between the condition of 100% and that of small fractional surface ionization. From the study of ion current-voltage curves obtained at or near this transition we were able to place rough limits on the threshold temperature, as indicated by the width of the shaded regions in Fig. 7. The multivalued ion currents near the threshold temperature have been observed and explained by Langmuir and others[12][13][14].

The Taylor-Langmuir saturation ion currents are plotted against our

reciprocal threshold temperatures for (100) and (110) tungsten in Fig. 10. Also shown are the threshold temperatures for polycrystalline tungsten as determined by Langmuir and Taylor. The ratio T_{EO}/T_{Cs} is a constant and equal to 3.5 for (100) tungsten and 3.8 for (110) tungsten. The higher ratio for (110) tungsten indicates a greater cesium adsorption potential than for (100) tungsten.

Conclusions

We have determined work functions for (100) planar tungsten for emitter temperatures from 850 to 1450°K and cesium-reservoir temperatures from 0 to 100°C. Work functions determined by electron-emission data agree within 0.03 eV with those determined from ion-emission data at emitter temperatures below the threshold ionization temperature. The threshold temperature occurs at an emitter-to-cesium-reservoir temperature ratio of 3.5 for (100) tungsten and 3.8 for (110) tungsten. Our measurements in planar geometry of saturated cesium-ion currents at 100% surface ionization as a function of cesium-reservoir temperature yielded currents 50% higher than those obtained by other investigators in cylindrical geometry with wire emitters. This is believed to result from differences in electrode geometries.

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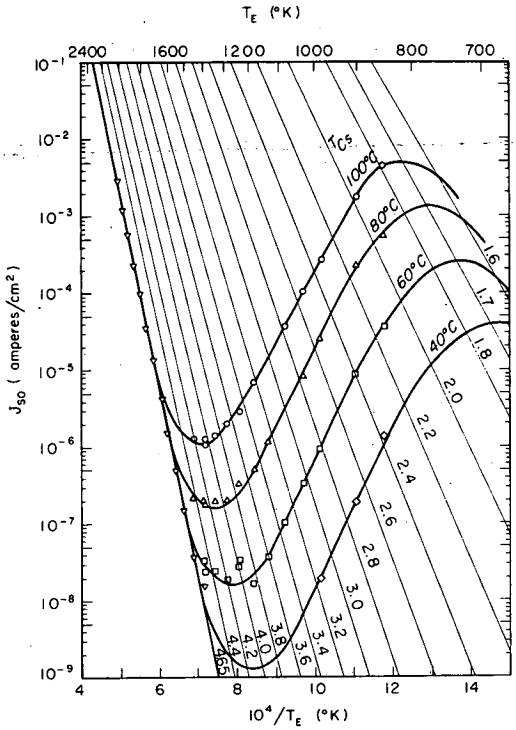

Fig. 1. Field-free saturated electron emission for (100) tungsten versus reciprocal emitter temperature $1/T_E$ for various cesium-reservoir temperatures T_{Cs}. The straight, sloping lines were calculated with the indicated work function and the experimental A(100) of 238 $A/cm^2 \cdot K^2$.

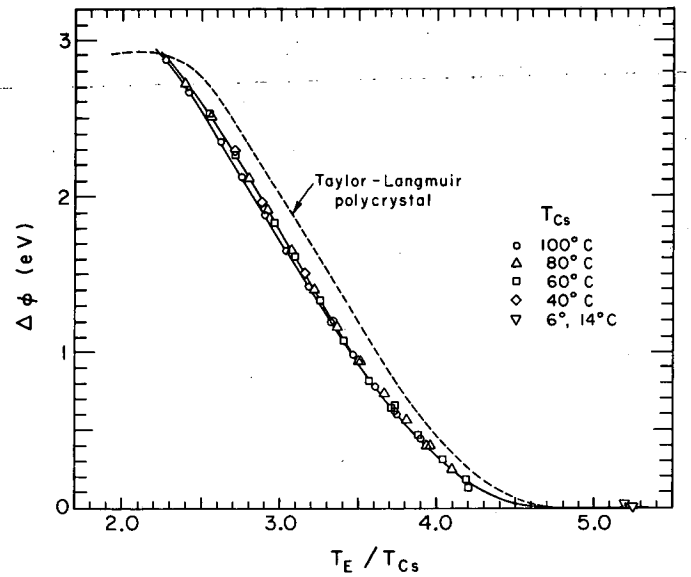

Fig. 2. Work function depression $\Delta\phi$ of the (100) emitter versus the emitter-to-cesium-reservoir temperature ratio T_E/T_{Cs}, determined from electron emission. The lower line was drawn through the data obtained at T_{Cs} = 100°C. The upper line is the best fit for the data obtained at all lower cesium temperatures. The dotted line shows the result obtained from the data of Taylor and Langmuir for polycrystalline tungsten. The bare work functions used in these curves were $\phi_0(100)$ = 4.65 eV, ϕ_0(Poly) = 4.62 eV.

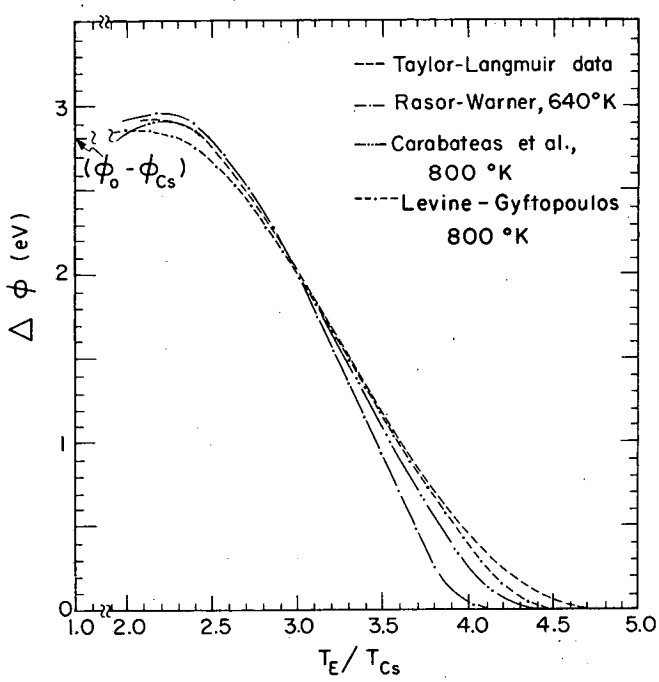

Fig. 3. Comparison of theory with Taylor-Langmuir data, normalized at $\Delta\phi$ = 2.0 eV.

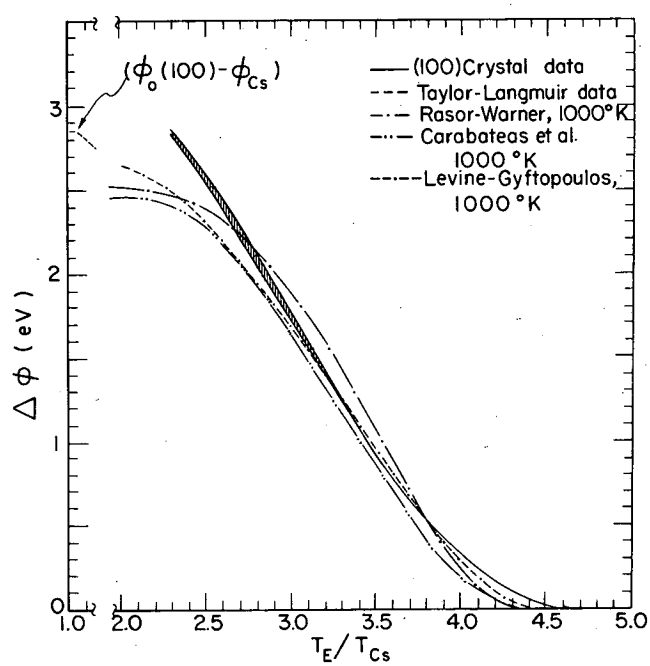

Fig. 4. Comparison of theory with (100) tungsten measurements [$\sigma(100) = 2.5 \times 10^{14}$ atom/cm^2].

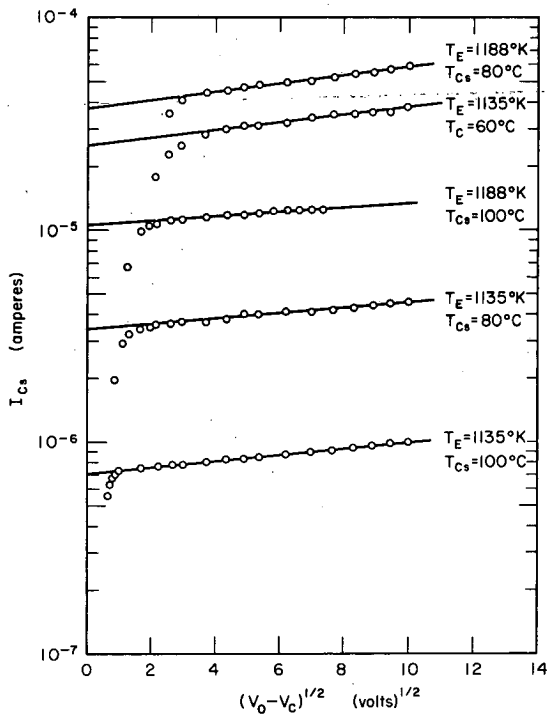

Fig. 5. Typical Schottkey plots of cesium-ion currents for (100) tungsten under conditions of low fractional ionization. V_C is the applied collector voltage and V_O is the contact potential.

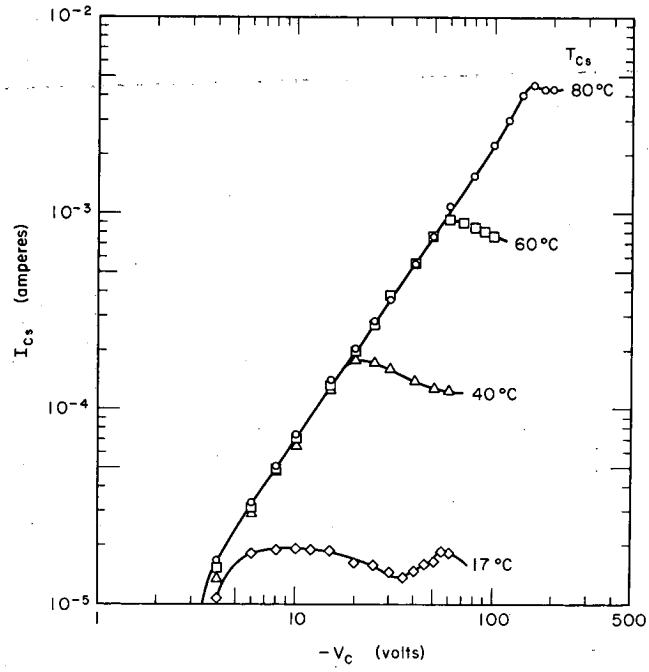

Fig. 6. Cesium ion current I_{Cs} versus applied collector voltage V_C for 100°% surface ionization, measured with the (100) diode at an emitter temperature of 1293°K and interelectrode spacing of 0.44 mm.

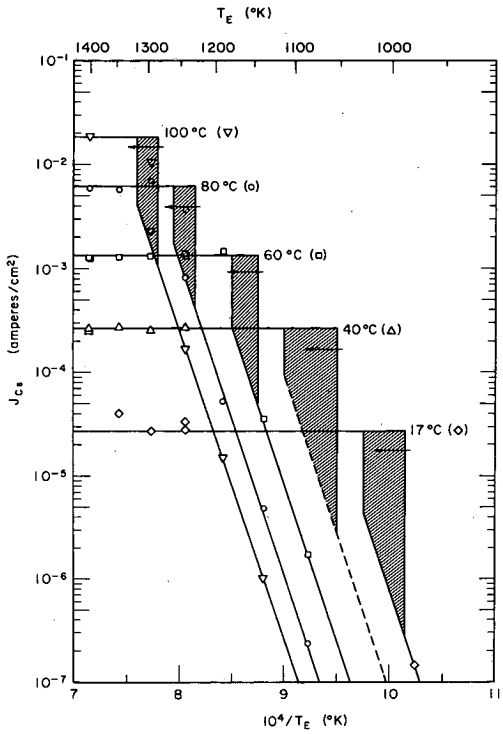

Fig. 7. Saturation cesium-ion emission for (100) tungsten versus reciprocal emitter temperature for various cesium-reservoir temperatures. The arrows indicate the cesium-ion current densities at 100% surface ionization measured by Taylor and Langmuir.

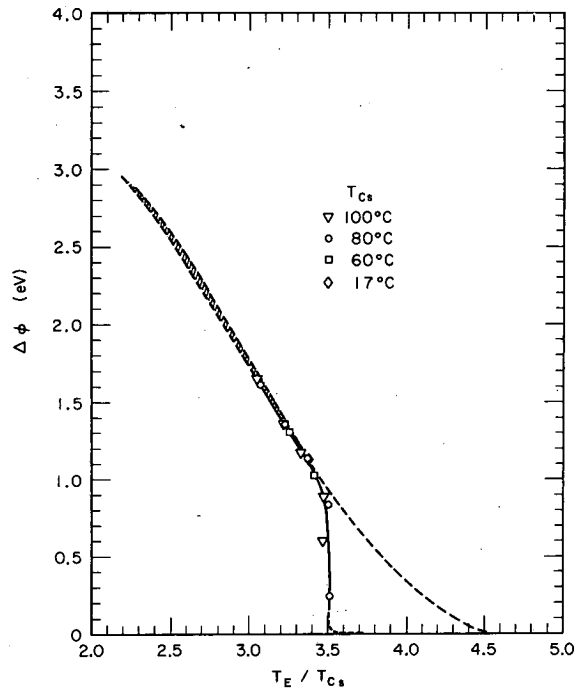

Fig. 8. Work function depression $\Delta\phi$ for (100) tungsten versus the emitter-to-cesium-reservoir temperature ratio T_E/T_{Cs}, determined from cesium-ion emission. The dotted lines show the corresponding result obtained from electron emission.

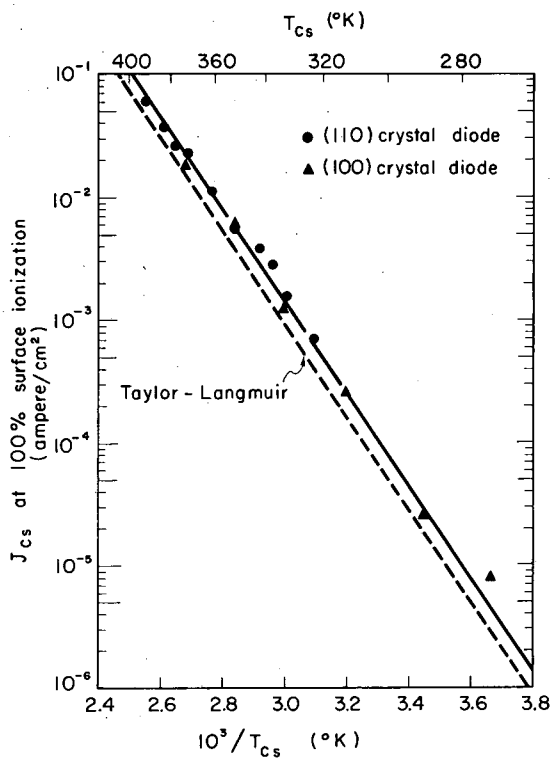

Fig. 9. Saturation cesium-ion current density I_{Cs} at 100% surface ionization versus reciprocal cesium reservoir temperature $1/T_{Cs}$.

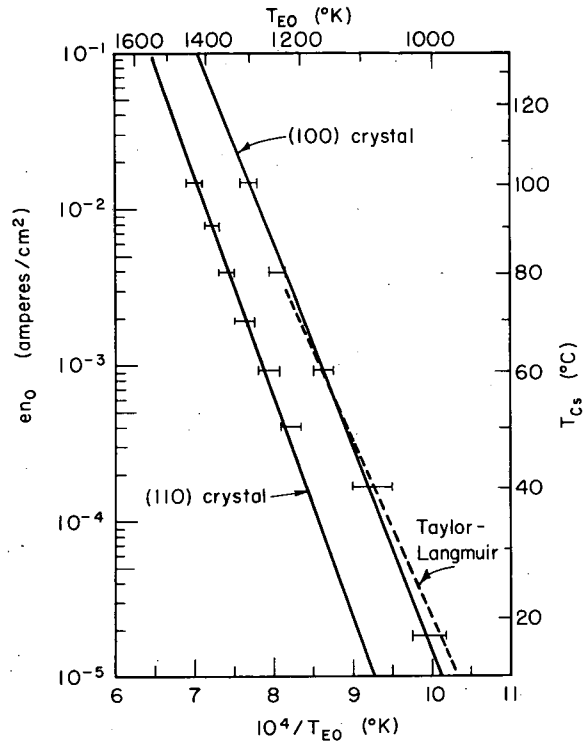

Fig. 10. Cesium-ion current density en_o at 100% surface ionization versus reciprocal threshold temperature $1/T_{Eo}$. The right ordinate T_{Cs} is the cesium reservoir temperature which gives rise to the cesium vapor flux en_o, as measured by Taylor-Langmuir.

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