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The Thermionic Emission and Work Function of U and UO_2

W. McLean
Hao-Lin Chen

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W. McLean and H.-L. Chen

University of California, Lawrence Livermore National Laboratory,

Livermore, CA 94550

ABSTRACT

Thermionic emission measurements have been used to determine the work function (Φ) of pure and oxidized uranium samples between 1100 and 1300 K; Auger electron spectroscopy (AES) was used to verify the cleanliness and compositions of the samples. It was found that impurities present in ppm amounts in the bulk U segregated to the surface upon heating and had an appreciable effect on the zero-field emission currents as well as the slopes of the Schottkey curves obtained at various temperatures. A combination of ion-sputtering and ultra-high vacuum (UHV) annealing at high temperatures was successful in reducing the total impurity level on the hot surfaces to ∿5%. At this low concentration of impurities, well-behaved Richardson line plots were obtained with $A = 135$ A cm^{-2} K^{-2} and $\Phi = 3.54$ eV for pure U, and $A = 128$ A cm^{-2} K^{-2} and $\Phi = 3.19$ eV for UO_2. The Schottkey coefficients for clean U approached their ideal values at fields > 400 V/cm.

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I. INTRODUCTION

The work function of uranium, especially in the region that is of the greatest significance for thermionic emitters (i.e., $T > 1050$K), is not well known. The state of knowledge on the work function of polycrystalline U is summarized in Table I.[1-11] Close examination of Table I shows that for γ-U the reported work-function values range from 3.18 to 3.60 eV. Various handbooks recommend values of 3.3 eV (Ref. 12) and 3.63 eV (Ref. 13). Some of this spread in data can be attributed to varying proportions of crystallites with different orientations; however, it is equally likely that the inconsistency is due to varying but unknown amounts of impurities on the surface. The work functions for epitaxial U films condensed on single-crystal faces of W are summarized in Table II.[14-16] For γ-U these values essentially covered the entire range reported for polycrystalline U in Table I. Note that most of the values listed in Table II refer to monolayers of U on W. Because of the size mismatch between the U and W atoms the fraction of the surface covered by U varies considerably. The most complete coverage occurs for monolayers on the (113) plane; hence it should be the most like U. We presume that for a sample annealed for long periods of time that densely packed low index planes of U would dominate the polycrystalline samples and we would anticipate a work function between 3.5 and 4.0 eV.

Few measurements have been performed on metallic U. Most have been for U films on W substrates. Another noticeable feature of Tables I and II is the apparent decrease in work function as U passed through the $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ phase transitions. This change was irreversible and has lead one set of authors to postulate that the change is more a characteristic of the U/W interaction than of bulk U itself.[17]

Table I: Summary of polycrystalline uranium work function data.

Ref.	Date	Method	T range (K)	A_R[a]	Φ_R(eV)	Φ_e(eV)	Description
1	1932	PE[b]	300			3.63	U film on Ni
2	1938	CP	300			4.32	U foil in Ar
3	1939	TE	950-1300	6	3.27	$3.27 + 2.55 \times 10^{-4}T$	U wire
4	1959	TE	1200-1550	114	3.47	$3.47 + 4.66 \times 10^{-6}T$	U film on W
5	1962	CP	300			3.08	U foil
		CP	300			3.19	U film on W
6	1962	PE	300-938			3.47	U foil
			938-1043			3.52	
			1043-1065			3.39	
7	1963	TE	1200-1700	8	2.90	$2.90 + 2.30 \times 10^{-4}T$	U film on W
8	1967	CP	300-950			3.63	U film on W
			950-1050			3.58	
			1050-1500			3.53	
		TE	1000-1400	80	3.42	$3.42 + 3.45 \times 10^{-5}T$	
9	1967	PE	400-950			3.65	U film on W
			950-1050			3.59	
			1050-1200			3.45	
10	1968	FE	300-940			3.60	U film on W
			950-1040			3.53	
			1050-1200			3.43	
11	1981	CP[c]	300			3.5 ± 0.1	U foil

[a] $A\ cm^{-2}\ K^{-2}$

[b] PE = photoemission, CP = contact potential difference, TE = thermionic emission, FE = field emission.

[c] Surface condition verified with XPS.

Table II: Summary of work function data for U on W single crystals.

Phase	α 300 <T< 940		β 950 <T< 1040		γ T> 1042	
Plane	**Φ(eV)**	**Method(Ref.)**	**Φ(eV)**	**Method(Ref)**	**Φ(eV)**	**Method(Ref)**
(100)	3.73 ± 0.02	CP(14)	3.61 ± 0.03	FE(15)	3.82 ± 0.03	FE(15)
	3.73 ± 0.02	PE(14)				
	3.78 ± 0.03	CP(14)				
	3.88 ± 0.03	FE(15)				
	3.80 ± 0.03	CP(16)				
(110)	3.90 ± 0.03	CP(14)	3.99 ± 0.03	FE(15)	4.00 ± 0.03	FE(15)
	3.90 ± 0.03	PE(14)				
	4.00 ± 0.04	CP(14)				
	4.04 ± 0.03	FE(15)				
	3.90 ± 0.03	CP(16)				
(111)	3.04 ± 0.03	FE(15)	3.36 ± 0.03	FE(15)	3.31 ± 0.03	FE(15)
(112)	3.70 ± 0.03	FE(15)	3.64 ± 0.03	FE(15)	3.29 ± 0.03	FE(15)
(113)	3.67 ± 0.03	CP(14)			3.53 ± 0.03	FE(15)
	3.66 ± 0.03	PE(14)				
	3.73 ± 0.04	CP(14)				
	3.60 ± 0.03	FE(15)				
(116)	3.57 ± 0.03	FE(15)			3.43 ± 0.03	FE(15)

All of the work functions obtained by the thermionic emission method exhibited a positive temperature dependence, whereas the work functions obtained by other techniques did not. The impact of the uncertainty in the work function on the thermionic emission current is illustrated by the shaded area in Fig. 1, where we see a spread of two orders of magnitude in this quantity.

It should also be noted that, with one exception,[11] all of the measurements in Tables I and II were done prior to the introduction of surface analytical methods capable of determining the true surface composition of the sample. Since the widespread introduction of these techniques it has been shown that very few metals can be effectively cleaned by simple heating and outgassing in UHV[18]; in fact, at elevated temperatures significant amounts of impurities present in ppm amounts in the bulk sample migrate to the surface region. This is particularly true of C, O, and S. It is clear that it is difficult to predict the thermionic emission current from U with any degree of certainty and for this reason we have chosen to reinvestigate this topic.

II. ANALYSIS

The current density produced by a thermionic emitter at a temperature T and an electric field E is given by the Richardson-Dushman equation modified to account for the Schottkey lowering of the potential barrier at the surface[19]:

$$J = AT^2 \exp(-e\Phi/kT) \exp(SE^{1/2}/T), \qquad (1)$$

where $A = 4\pi mek^2/h^3 = 120$ A cm^{-2} K^{-2}, Φ= work function in eV, $S = e^{3/2}/k = 4.403$ K for E in V/cm, and $e/k = 11{,}606$ deg/eV.

The first step in deriving the work function is to determine the zero-field current. This can be done for uniform surfaces at low-field by neglecting the term $\exp(SE^{1/2}/T)$ in Eq. (1) and noting the departure of the saturation current from the space-charge line.

Alternatively Eq. (1) can be rearanged as:

$$\ln(J) = SE^{1/2}/T - e\Phi/kT + \ln(AT^2). \qquad (2)$$

From Eq. (2) it can be seen that a plot of $\ln(J)$ vs $E^{1/2}$ at a given T yields a straight line with a slope of S/T and an intercept of $\ln(J_0)$. If S is less than 2X the theoretical value the error introduced to J_0 by the extrapolation to zero field is negligible.[19] For polycrystalline surfaces, measurements at high fields tend to weight low work-function facets more heavily in the average work function, whereas at low fields the measured work function reflects the average Φ of the surface.[20]

To calculate the work function one can assume the ideal value of $A = 120\ \mathrm{A\ cm^{-2}\ K^{-2}}$ and solve Eq. (1) at zero field for:

$$\Phi_e = -\ln(J_0/120T^2)kT/e, \qquad (3)$$

where Φ_e is the effective work function. A more rigorous approach is to rearrange Eq. (1) at zero field as:

$$\ln(J/T^2) = \ln(A) - e\Phi/kT. \qquad (4)$$

By plotting $\ln(J/T^2)$ vs $1/T$ one obtains the so-called Richardson plot whose slope is $-e\Phi/k$ and whose intercept is $\ln(A)$. The constants obtained by this treatment are generally denoted as Φ_R and A_R. Since A_R

is obtained from rather long extrapolations to $1/T = 0$, it is necessary to obtain very good values of J_0 over a long range of T to get an accurate value for the Richardson constant. The values of A_R in Table I range from 6 to 114 A cm^{-2} K^{-2}.

The constants A and A_R are related to each other as follows. For the Richardson line to be straight over a given temperature range, the work function must exhibit temperature-dependent and independent parts, i.e. :

$$\Phi = \Phi^0 + d\Phi/dT. \qquad (5)$$

If this expression is inserted into Eq. (1) at zero field, we obtain

$$J = AT^2 \exp(-e\Phi^0/kT) \exp(-e/k \; d\Phi/dT). \qquad (6)$$

If we let $\Phi^0 = \Phi_R$, then:

$$A_R = A \exp(-e/k \; d\Phi/dT). \qquad (7)$$

The thermionic-emission derived work functions in Table I are listed both in the Richardson form and as effective work functions. Note that for $A_R < 120$ the effective work function increases with temperature, for $A_R \sim 120$ the effective work function is a flat function of temperature, and for $A_R > 120$ the effective work function will decrease with temperature.

III. EXPERIMENTAL

The measurements described below were performed in a stainless steel vacuum chamber with a base pressure of 5×10^{-11} Torr. Samples were prepared by machining a cap out of depleted U with a total impurity content of less than 30 ppm. The surface of the cap was polished to a mirror finish with a series of progressively finer diamond abrasives down to a surface roughness of 0.25 μm. The sample was then fitted over a 50-W Mo-jacketed resistance heater (see Fig. 2). Since Mo is known to diffuse readily into U at 1070 K,[21] a thin layer of MgO in methanol was applied to the inside of the U cap. This coating prevented direct U/Mo contact and prevented alloying even when the sample was heated to 1370 K for several days.

Temperature was the most critical variable to monitor because it appears in Eq. (1) a total of 4 times. It was monitored with a W-5%Re/W-26%Re thermocouple pair spot welded to the U cup. In the event of a thermocouple failure another determination of temperature could be obtained by monitoring the radiation from a blackbody consisting of a thin layer of colloidal graphite applied to the side of the sample. The measurement was made with an optical pyrometer having a calibration traceable to NBS. The window and emissivity corrections for the pyrometer were established prior to thermocouple failure by correlating the pyrometer output with the thermocouple readings. The thermocouple was in turn calibrated to the known phase tranisitions of U. When heating the samples at constant power, a 10-20 s thermal arrest occurred at the $\alpha \rightarrow \beta$ (941 K) and $\beta \rightarrow \gamma$ (1048 K) phase transitions since these changes required considerable heat input (0.665 and 1.165 kcal/mole, respectively). When power was removed from the sample, it generally fell below the phase transition temperature prior to the onset of an exothermic recalescence reaction during which the temperature once again rose to the phase transition temperature before decreasing further. This change was the most noticeable for the $\gamma \rightarrow \beta$ transition. The best results

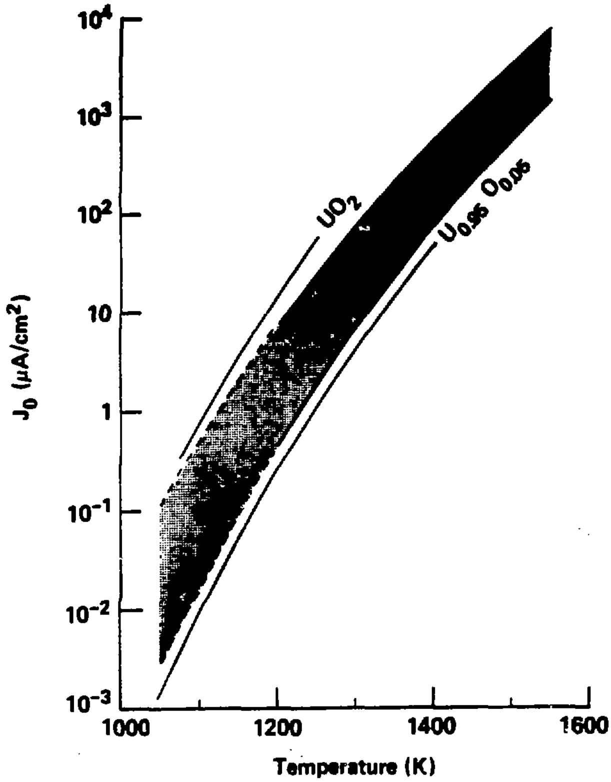

Fig. 1. Range of reported thermionic emission currents for U. Solid lines are from this work.

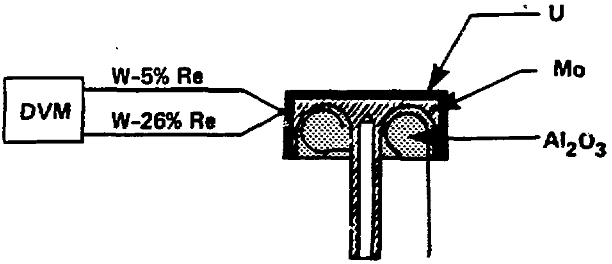

Fig. 2. Sample mounting for U and heater.

were obtained with 0.0078 cm diam thermocouple wires since these did not provide an appreciable heat sink and exhibited no thermal inertia. The agreement between the thermocouple readings and the recorded phase transitions was ±1 K, the agreement between the thermocouple and the pyrometer was ±2 K. Occasionally one of the sample caps was deliberately melted to provide a third calibration point. The pyrometer was also used to assure that the sample temperature was uniform. Temperature changes across the surface were less than the 2 K readability of this instrument.

The cleaning procedure used in UHV was adapted from those found in *Refs. 18 and 22 and was as follows:*

1. Remove gross contamination by argon ion sputtering at 5 keV, 20 μA/cm^2, and ambient temperature.
2. Deplete bulk impurities by continued sputtering at 1300 K.
3. Anneal at 1300 K in UHV for 15 min.
4. Repeat steps 2. and 3. until the surface could be maintained for 30 min without further impurity segregation.
5. Subsequent *environmental contamination could be removed* by 30-60 s of argon ion sputtering at 2 keV and 5 μA/cm^2.

Oxygen and carbon were the most persistent contaminants on the surface at all temperatures, although the relative amount of carbon generally decreased with increasing temperature.

The atomic composition of the surface was determined by Auger electron spectroscopy using standard analytical techniques. The atomic sensitivity factors (ASF) for most of the common elements were obtained from Ref. 23, while that for the U(NOO) doublet was deduced from UO_2 (see results). Auger spectra were taken before and after each thermionic-emission measurement. The spectra were obtained with a single-pass cylindrical mirror analyzer (CMA) with an internal electron gun operating with a beam voltage of 3 keV and a current of 20 ± 5 μA. Spectra were obtained in the dN(E)/dE mode by applying a 6-V modulation to the CMA.

Thermionic emission currents were measured as a function of applied field with the circuit illustrated in Fig. 3. The anode consisted of a shielded collector having an inner probe with an area of 0.2235 cm^2 operating at the same applied voltage as a concentric guard ring to provide a uniform field over the region being measured. The voltage source was either a battery or a low-impedance power supply. The anode-cathode spacing was measured from outside the vacuum system with a telescope-mounted cathetometer and was generally 0.30 ± 0.05 cm. The emission current was measured with an ammeter using a current follower preamplifier in order to minimize the voltage drop through the meter. An analysis of the probable errors in measuring the temperature (± 5 K), probe area (±0.0025 cm^2), current (± 0.2% full-scale reading), and anode-cathode spacing (±0.05 cm) lead to a worst case error stack-up of ±0.03 eV in Φ and ±10% in S.

IV. RESULTS

The Auger spectrum of a U surface on outgassing 10 hours in a vacuum of 2×10^{-10} Torr at 1250 K is illustrated in Fig. 4 (a). At this point the surface C and O layers were removed by a brief period of argon-ion sputtering, then heated in UHV for another 100 h. This procedure was similar to that used in Refs. 3, 4, and 6, but the duration was a factor of 10 shorter in our case. We do not feel that holding the sample at 1250 K for another 900 h would have affected the surface composition in a positive way. The surface composition at this point was approximately US_2 [see Fig. 4 (b)]. Only after more than 100 h of sputtering at 1300 K

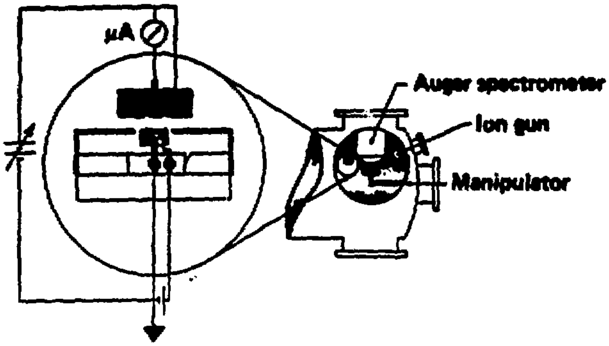

Fig. 3. Experimental setup showing vacuum chamber and measuring circuit.

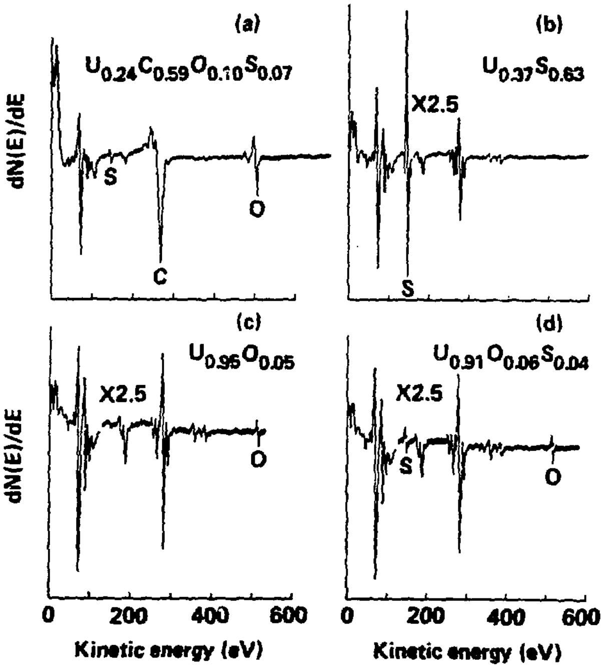

Fig. 4. Auger spectra of U sample: (a) U heated to 1300 K in UHV for 10 h; (b) U after removing surface layer of C and O, then heating at 1300 K for 100 h; (c) U after 100-h Ar-ion sputtering (5 keV, 20 μA/cm^2, 1300 K); (d) "clean" U after residing in UHV for 1 h at 1300 K.

were we able to deplete this contaminant sufficiently to prevent its reappearance for periods of time long enough to perform useful measurements [Fig. 4 (c)]. If the samples were left in UHV long enough at elevated temperatures, the S would invariably return [Fig. 4(d)].

Oxygen was particularly persistent and we were not successful in reducing it to less than 5 atom % on hot surfaces. The Ar introduced into the chamber for sputtering was purified in a Ca-lined furnace,[24] was monitored with a quadrupole mass spectrometer, and was found not to contain any oxygenated species. Since we could eliminate this contaminant from the surface at low temperatures, we believe its presence to be caused by migration from the bulk material or by reaction of the hot surface with residual CO in the vacuum chamber. Our difficulty in controlling the surface purity in a good vacuum further emphasizes the significance of the absence of information on the surface composition for previous U work-function measurements.

Figure 5 shows the Auger spectrum of U that was deliberately oxidized at ambient temperature in 5 X 10^{-5} Torr of O_2 for approximately 30 min. Other authors[25] have shown that this procedure will produce nearly stoichiometric UO_2. The atomic sensitivity factor (ASF) for the U(NOO) doublet at 186 eV in our Auger spectrometer was deduced by assuming this species to be UO_2 and using the ASF for O listed in Ref. 23. Thus we were able to deduce the approximate compositions of the surfaces whose spectra are shown in Fig. 4.

The low-field current vs voltage measurement for nearly clean U at 1275 K is shown in Fig. 6 (a). Extrapolating to zero field yielded an effective work function of 3.53 eV. A family of Schottkey plots for clean U at various T's is shown in Fig.7. Note that the Φ_e at 1275 K is also 3.53 eV [Fig. 7 (b)] and a Schottkey coefficient S of 0.0070

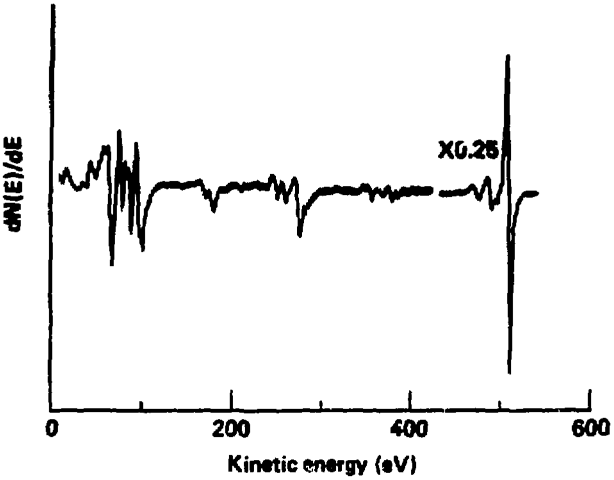

Fig. 5. Auger spectrum of $UO_{(2.0 \pm 0.2)}$

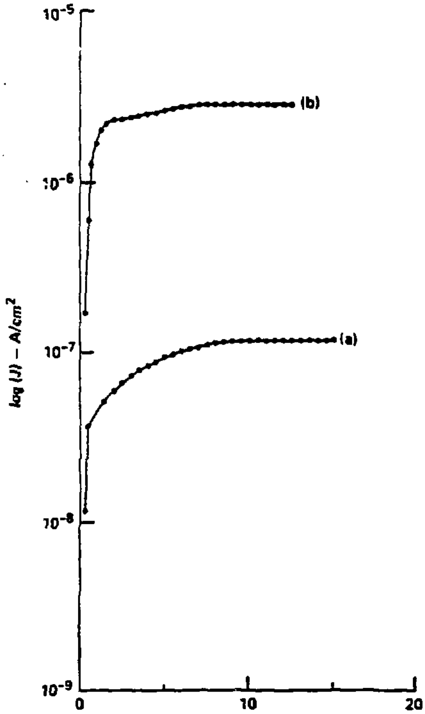

Fig. 6. Low-field current vs voltage for (a) $U_{0.95}O_{0.05}$ and (b) UO_2.

(approximately 2X the theoretical value of 0.0035) was obtained for fields greater than 400 V/cm. Figure 8 (a) shows the Richardson plot obtained for a series of J_0/T^2 values obtained in this manner for $U_{0.95}O_{0.05}$. For nearly clean U the Richardson constant A_R was 135 A cm^{-2} K^{-2}, in good agreement with the ideal A value. The value of Φ_R was 3.54 eV, which was also in good agreement with the values obtained as Φ_e(3.53 ± 0.01 eV), implying that there was little, if any, temperature dependance in the U work function; it is also in good agreement with the contact potential difference value obtained by Barry et al.[8] The fact that the same answer was obtained at low field and from extrapolation of the Schottkey plots implies that the sample surfaces were indeed uniform. The impact of this new emission constant and the work function on the thermionic emission current is illustrated by the lower solid line in Fig. 1.

The departure of the emission current from the space-charge line for UO_2 at 1275 K is illustrated in Fig. 6 (b). Note that it was difficult to produce and maintain a UO_2 surface in the 1100-1300 K range as O tended to disappear from the U surface at these temperatures. High doses of O_2 (> 8000 Torr sec at 1275 K) were needed to produce surfaces with Auger spectra similar to Fig. 5. For this reason there was much more scatter in the UO_2 work-function data and only low field measurements requiring 2 to 3 s measurement times were performed. A Richardson plot of J_0/T^2 values obtained over a range of T's is shown in Fig. 8 (b). A_R was 128 A cm^{-2} K^{-2} and Φ_R was 3.19 eV. These values gave good agreement with Φ_e = 3.20 ±0.02 eV. The impact of these values on the thermionic emission current is shown by the upper line in Fig. 1.

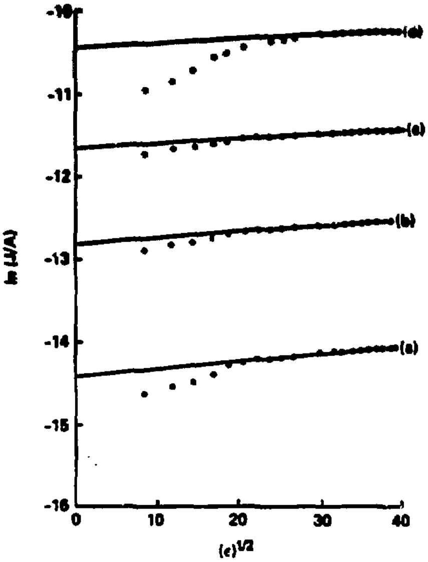

Fig.7. Schottkey plots for $U_{0.95}O_{0.05}$ at various temperatures: (a) 1232 K; (b) 1275 K; (c) 1326 K; and (d) 1360 K.

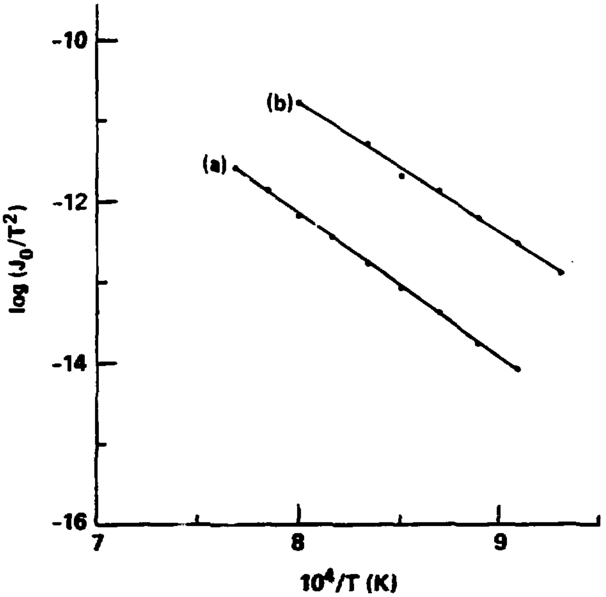

Fig. 8. Richardson plot for (a) $U_{0.95}O_{0.05}$ and (b) UO_2.

V. DISCUSSION

The fact that all of the previously reported thermionic emission currents lay between the limits defined in this work by $U_{0.95}O_{0.05}$ and UO_2 indicates that the older measurements were performed on partially contaminated surfaces. A review of the vacuum conditions and the periods of time during which samples resided in vacuum at elevated temperatures lends credence to this interpretation. The thermionic emission current from our cleanest sample should be considered as an upper limit to the thermionic emission from clean uranium. Although quantitative measurements of $\Delta\Phi$ vs oxygen coverage for uranium have not yet been performed, Riviere has shown that Φ does decrease rapidly with oxygen exposure.[26] An estimate to the magnitude of this effect for 0.05% oxygen content can be obtained by comparison to $\Delta\Phi$ measurements for O on Th, where it was found that contamination by a similar amount of oxygen lead to a $\Delta\Phi$ of -0.15 ± 0.05 eV.[27]

In summary, the thermionic emission current of nearly clean U ($U_{0.95}O_{0.05}$) has been measured over the temperature range 1075 - 1350 K and found to fit the curve:

$$J = 135T^2 \exp(-3.54\text{eV}/kT) \exp(8.8E^{1/2}/T). \qquad (8)$$

At zero field nearly stoichiometric UO_2 was found to fit the curve defined by:

$$J = 128T^2 \exp(-3.19\text{eV}/kT). \qquad (9)$$

In both cases there was no apparent temperature dependence exhibited by the work function.

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