

# PHYSICAL REVIEW B

## CONDENSED MATTER

THIRD SERIES, VOLUME 27, NUMBER 7

1 APRIL 1983

### Positron and positronium emission from tungsten (111)

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(Received 10 June 1982; revised manuscript received 27 December 1982)

We present new experimental results on positron interactions with clean tungsten (111) single crystals. The measured value of the positron work function is  $\phi_+ = -2.59(10)$  eV, which implies a negative work function for positronium and its negative ion as well. The observed yield, which is defined as the fraction of slow positrons reemitted from the sample, is 41% for 1-keV incident beams, and high yields are expected for incident radioactive source  $\beta^+$  because of the small  $\beta^+$  penetration depth. The yield is limited by positronium formation and trapping into a surface state bound by  $E_B = 2.81(10)$  eV. Positron surface interactions for W(111) appear similar to other clean crystalline metals with the exception of the broad energy distribution of emitted positrons which appears not to be caused by surface contamination. Difficulties associated with this energy width can apparently be overcome by growing thin epitaxial Cu films on the W(111) surface, as suggested by Lynn and Lutz [Phys. Rev. B 22, 4143 (1980)], and may result in an efficient, bright, slow-positron source.

#### I. INTRODUCTION

The rapidly developing field of slow-positron physics owes much to continuing progress in the development of intense monochromatic beams of low-energy positrons. Such beams are useful for bulk<sup>1</sup> and surface<sup>2</sup> defect studies and may prove valuable for surface characterization<sup>3,4</sup> if sufficiently intense sources become available. Presently most slow-positron studies utilize a radioactive  $\beta^+$  source to bombard a moderating material having a negative positron affinity.<sup>5</sup> Incident high-energy positrons thermalize rapidly in the bulk and a small fraction stop sufficiently near the surface that they may diffuse back to the interface and be emitted before annihilating in the solid. The efficiency of a moderator clearly depends on the positron work function ( $\phi_+$ ), characteristic bulk stopping and diffusion lengths, and on the interactions of thermalized positrons at the surface. High-density moderator materials with short  $\beta^+$  stopping lengths may prove useful for increasing beam intensities provided the slow-positron yield and emission spectrum are suitable. Previous theoretical work<sup>6</sup> shows that tungsten has a large negative  $\phi_+$  and polycrystalline tungsten foils have been used successfully as slow-positron moderators.<sup>7</sup> To better understand positron surface interactions we have characterized slow-

positron emission and thermal activation of positronium formation from atomically clean single-crystal W(111) faces. Only two other metals, Cu and Al, have been studied previously in this way<sup>8,9</sup> and our observations of W(111) reveal some unusual features. We have also attempted to observe emission of  $\text{Ps}^-$  from the W(111) surface without success.

#### II. EXPERIMENTAL APPARATUS

Positrons are obtained from approximately 100 mC of  $\text{Co}^{58}$  electroplated on a tungsten sheet which irradiates a backscattering Cu(111) + S moderator described earlier.<sup>10</sup> The resulting slow positrons are accelerated by a variable beam voltage and conducted along the axis of a 150-G magnetic solenoid into a UHV sample chamber operating at pressures in the  $10^{-10}$  Torr range. Figure 1 shows the sample chamber equipped with low-energy electron diffraction (LEED) or Auger-electron spectrometer, an Ar-ion gun, a system of grids for energy analysis of the emitted positrons, and filaments for heating the sample by electron bombardment. Positron annihilation  $\gamma$  rays are detected with NaI scintillation detectors whose output may be counted and integrated to determine the energy of the incident gamma ray. Data is recorded on a multichannel analyzer and transferred to magnetic tape for subse-

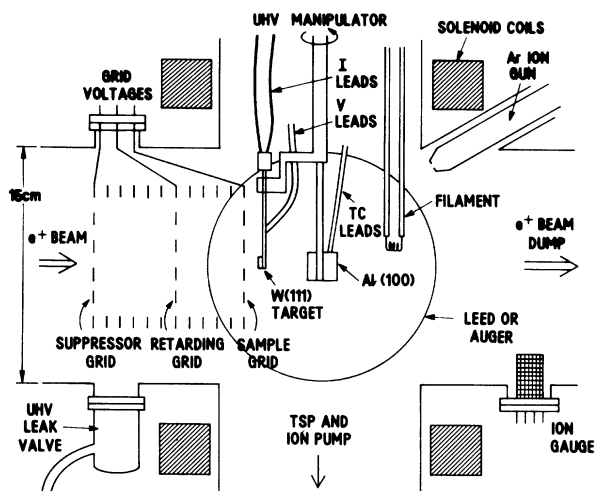


FIG. 1. Sample chamber for cleaning and characterizing single-crystal metal surfaces of W(111) and Al(100). The sample and suppressor grids are biased to direct emitted positrons back down the beam line for  $\phi_+$  measurements and energy analysis by the retarding grid occurs in a uniform-field region. The sample grid is biased positive with respect to the sample in positronium thermal activation measurements.

quent analysis.

The sample is a 7-mm diam. tungsten (111) crystal oriented to within  $\frac{1}{2}^\circ$  by Laue x-ray scattering and cut 1 mm thick by spark erosion. After mechanical lapping to a mirror-finish surface flat to within a few degrees and electropolishing in NaOH solution the crystal is spot welded to two 25-mil (1 mil =  $10^{-3}$  in.) tungsten wire leads which are attached to the manipulator and conduct heating currents through the sample. Two additional 5-mil tungsten leads are spot welded to the heater wires near the sample to allow measurements of the voltage drop as a function of heater current. The current leads heat to temperatures closely equal to the sample up to their junction with the voltage leads. Temperatures are computed by assuming that sample resistance is linear in  $T$  and calibrated with an optical pyrometer at the maximum temperature (1100 K) obtained by resistive heating.

Preparation of clean W(111) surfaces is complicated by the solubility characteristics of carbon. High-temperature (2600°C) flashing by electron bombardment rapidly reduces the initial carbon coverage to submonolayer proportions by activating diffusion into the bulk.<sup>11</sup> Sharp LEED patterns characteristic of the W(111) surface are obtained and the "square" LEED pattern, attributed to ordered carbon overlayers,<sup>12</sup> is not observed. Heating in oxygen is effective in reducing both bulk and surface carbon<sup>13</sup> but is known to cause facets on the

W(111) surface.<sup>14,15</sup> These facets can be annealed out by flashing to 2600°C but the Auger-electron spectrum shows detectable carbon coverage [ $\leq 0.1$  monolayer ML] following such annealing cycles, even after oxygen treatment or iron bombardment. We have obtained carbon-free surfaces ( $\leq 0.02$  ML) by heating to approximately 1200°C in  $< 10^{-7}$  Torr oxygen and continuously monitoring the Auger spectrum. When the carbon signal disappears oxygen is removed and the sample temperature raised slowly to volatilize surface oxides.<sup>16</sup> This procedure has been used previously with an alternative method for removing oxygen<sup>17</sup> but surface conditions such as microscopic roughness are uncertain. An oxygen-covered surface has been obtained by continuing oxygen exposure at room temperature after the carbon-removal process. We have not LEED characterized this surface, which shows many stable structures depending on adsorption and annealing temperatures.<sup>18</sup> Positron measurements have been made on submonolayer carbon-contaminated surfaces which give sharp LEED patterns without spots associated with faceting and on oxygen-saturated surfaces described above.

### III. RESULTS

Positron work functions are obtained by energy analyzing positrons emitted from the sample.<sup>8</sup> The W(111) crystal is positioned in the incident beam a few mm from a sample grid biased 8 V negative with respect to the sample to eliminate the effects of weak stray potentials. Positrons are accelerated through the sample grid and energy analyzed by a variable voltage  $V_R$ , applied to the retarding grid. Those with sufficient energy traverse the retarding grid and return along the beam line to an  $\vec{E} \times \vec{B}$  filter where they are deflected into the walls. Positrons reflected by the retarding grid return to the sample at low energy and ultimately result in annihilations which are recorded as a function of retarding grid voltage. Positron emission results in a decline in count rate which approximately represents the yield of slow positrons emitted with parallel energy  $E_z = \frac{1}{2} MV_z^2 > e(V_R - V_0)$  at a fixed incident beam energy  $E_B$ . The constant  $V_0$  absorbs the sample bias voltage and contact potentials between the retarding grid and sample.

Results for a nearly clean W(111) surface, contaminated with  $< 0.1$  monolayers of carbon, and for a saturated oxygen overlayer are given in Fig. 2. The positron work function is taken to be the voltage difference between the point where the count rate drops most steeply, when only the highest-energy reemitted positrons can escape, and the point where all positrons escape. We obtain

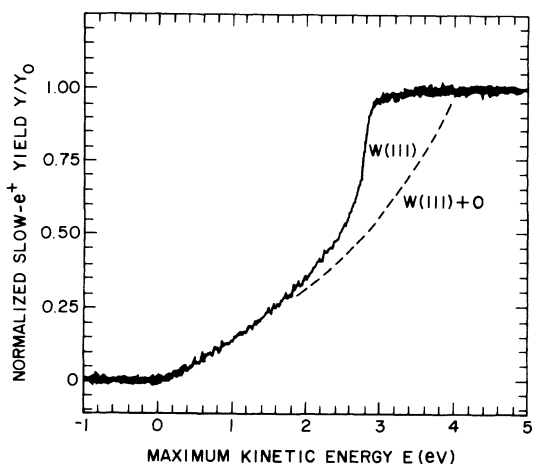


FIG. 2. Normalized integral parallel energy spectra of W(111) and W(111) + O. This data gives the relative number of positrons emitted with kinetic energies less than  $E$  for a 1-keV incident beam. The total yields are 41% and 53%, respectively.

$\phi_+^c = -2.64(10)$  eV for the  $<0.1$  ML carbon-contaminated W(111) surface and  $\phi_+^0 = -4.0$  eV for the oxygen-covered surface. To obtain a value of  $\phi_+$  for the atomically clean W(111) surface, where the electron work function is known, we have made simultaneous measurements, shown in Fig. 3, for a heavily contaminated W(111) surface and a clean sputter-annealed Al(100) surface. The difference between the voltages which just allow all emitted  $e^+$  to escape is equal to the difference of electron work functions of the respective crystal faces and is measured to be  $0.77(10)$  eV. From the known<sup>19</sup> clean-surface electron work functions  $\phi_-[\text{Al}(100)] = 4.41(3)$  eV and  $\phi_-[\text{W}(111)] = 4.47(2)$  eV we may deduce the value of the dipole layer of the contaminating overlayer,  $D = 0.71(10)$  eV, by using the relationship  $\phi_-^c = \phi_- + D$ .<sup>20</sup> The positron work function  $\phi_+^c = -3.30(10)$  for the contaminated surface is obtained by the same method as before and the clean-surface value is  $\phi_+ = \phi_+^c + D = -2.59(10)$  eV. Using the clean-surface positron and electron work functions we may compute work functions for Ps and  $\text{Ps}^-$  as well. The Ps work function is insensitive to surface contamination as the dipole layer cancels in the relationship  $\phi_{\text{Ps}} = \phi_+ + \phi_- - (1 \text{ Ry})/2n^2$  for Ps of principal quantum number  $n$ . We find that ground-state Ps emission is possible,  $\phi_{\text{Ps}} = -4.92(10)$  eV, but excited Ps cannot be formed from thermalized bulk positrons. The work function of the recently discovered  $\text{Ps}^-$  ion<sup>21</sup> is found by using the calculated binding energy<sup>22</sup>  $E^* = 0.327$  eV of the extra electron in  $\phi_{\text{Ps}^-} = \phi_{\text{Ps}} + \phi_- - E^* = -0.79(10)$  eV. This result indicates that  $\text{Ps}^-$  for-

mation is marginally allowed and more energetically favorable if the electron work function is reduced through surface adsorbate coverage.

Our measurements of positron work-function shifts induced by surface adsorbates can be compared with existing data for electron work functions. The contact-potential difference between a clean W(111) surface and a  $p(1 \times 2)$  oxygen-covered surface has been previously measured as 1.36 eV.<sup>15</sup> Repeated thermal cycling and continued oxygen exposure increases this shift to +2.06 eV. The oxygen-induced shift for the positron work function is measured to be -1.4 eV, in reasonable agreement with the  $p(1 \times 2)$  overlayer anticipated. Methane adsorption at elevated temperatures where carbon is the only surface species induces a +0.2-eV electron work-function change,<sup>1</sup> also in reasonable agreement with other measurements for  $\sim 0.5$  ML carbon-contaminated surfaces.

The slow-positron yield  $y$  can be obtained approximately by computing the fractional change in count rate between large positive and negative retarding grid voltages. This change represents annihilations of low-energy positrons which have been emitted and returned to the sample by the retarding grid after passing through the nominally 95% transmission sample grid. These particles have energies comparable to  $-\phi_+$  and do not penetrate substantially into the bulk but they may be reflected from the surface to repeat the cycle, trapped in the surface state, or escape from the surface as positronium. Triplet Ps poses a difficulty for accurately es-

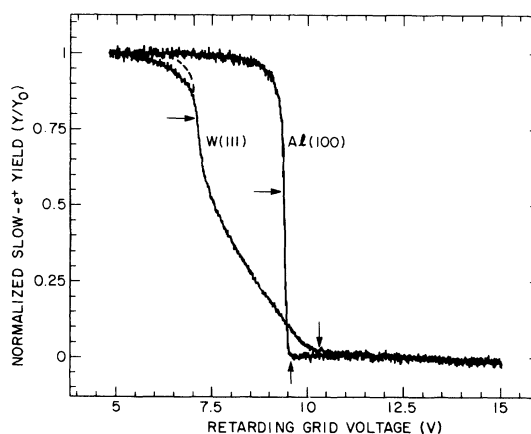


FIG. 3. Slow-positron emission spectra for W(111) and clean Al(100) obtained under conditions where the retarding grid work function does not change. The electron work-function difference is measured between the vertical arrows and the positron work-function difference from the horizontal arrows. The dashed curve represents the sharpening of the distribution at higher incident energies, the data presented is for 500-eV incident positrons.

timating the yield because its three-photon decay gives this annihilation mode an energy spectrum and counting efficiency different from two-photon decays. If the triplet positronium branching ratio varies with incident energy then the counting efficiency for slow  $e^+$  returned by the retarding grid will be different from that of the initial beam and result in a systematic error in the yield. A background subtraction is also necessary to account for annihilations detected from Ps or when incident or emitted positrons are intercepted by the proximal sample grid. An estimate of this latter background can be obtained by using low-energy incident  $e^+$  under bias conditions where the incident beam is reflected by the sample potential after passing through the grids. Counts recorded with this arrangement represent annihilations of low-energy positrons making a double pass through the grids and amount to 10% of the counts obtained when all positrons in the beam annihilate. The grid background correction is therefore obtained by assuming that 95% of the incident flux reaches the sample and 95% of the resulting emitted positrons escape through the grids. To check for possible anomalies associated with Ps emission we have made work-function measurements by energy-analyzing annihilation photons and counting only those events which fall within spectral regions where triplet Ps appears. Counts recorded in the energy ranges near the photopeak or below the photopeak and above the Compton edge agree to within 5% so that triplet Ps formation evidently proceeds with similar efficiency for initial keV and recollected low-energy positrons. We estimate the background-corrected yields for clean- and oxygen-covered tungsten (111) surfaces to be 0.40(0.05) and 0.53(0.05), respectively, with estimated uncertainties which should allow for triplet Ps counting efficiency or wall-induced spin-exchange corrections. These values are comparable to Cu(111) + S and higher than Cu or Al.<sup>8</sup> Carbon contamination at levels  $\sim 0.5$  ML reduces the yield by  $< 10\%$ .

Emitted positron differential parallel energy spectra are indicated in Fig. 4 for two runs where the surface normal is aligned at  $0^\circ$  and  $30^\circ$  to the axial magnetic field. The distribution is quite broad and poses difficulties for high-resolution studies. The peak should shift as  $\phi_+ \cos^2 \theta$  for narrow-beam emission<sup>20</sup> but the experimental peak for  $30^\circ$  falls somewhat higher than  $0.75\phi_+$ . The width of the distribution decreases the brightness, defined as the peak value of  $\partial y / \partial E_z$ , of W(111) to well below that of either Cu or Al. A further reduction in brightness results if the crystal is tipped or oxygen adsorbed. If a few eV spread in positron energies is deleterious to a particular experiment it may be preferable to use materials which give much sharper distributions at

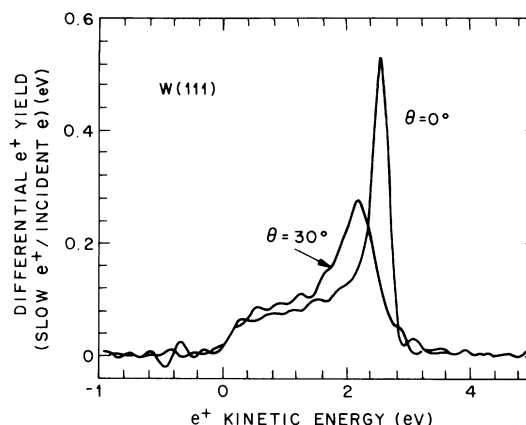


FIG. 4. Differential parallel energy spectra for a clean W(111) surface inclined at  $0^\circ$  and  $30^\circ$  with respect to the retarding grid with a 1-keV incident beam.

reduced yields. Moderator geometry is evidently an important factor as surfaces normal to the beam direction give substantially better results.

The value of W(111) as a slow-positron source depends critically on the fraction of the source  $\beta_+$  spectrum which is moderated. If the yield is measured for various incident beam energies one can determine this fraction accurately for a given radioactive source. Previous efforts along this line have described the energy-dependent yield as  $y(E) = y_0(1 + E/E_0)^{-1}$ . We find that increasing the beam energy from 1 to 3 keV results in a 10% decrease in  $y$ . This gives  $E_0 = 25(5)$  keV, which is a significant improvement over Cu (8 keV) and Al (2.9 keV).<sup>8</sup> Recent results<sup>23</sup> show that this parametrization of  $y(E)$  is incorrect and overestimates the high-energy yield. We cannot therefore reliably extrapolate our data to high energies but it does appear that W moderators should harvest more of a radioactive source  $\beta^+$  spectrum than Cu. The only disadvantage of W(111) is the extreme width of the emitted positron spectrum. We have attempted to overcome this difficulty by evaporating Cu onto W(111) *in situ* as suggested by Lynn and Lutz.<sup>24</sup> Figure 5 shows the emission spectrum before and after the evaporation onto the room-temperature crystal. The Cu overlayer appeared absorptive at first but strong sharp emission resembling that of single crystal Cu(111) was obtained after annealing. The work function and yield observed suggest little surface sulphur contamination. Annealing at higher temperatures gave a broad triangular spectrum which could result if the overlayer is too thin to thermalize positrons emitted from the W(111) crystal. The observed spectrum is quite similar to that of oxygen-covered tungsten and may simply represent the effect of  $\cong$  monolayer Cu. The overlayer thick-

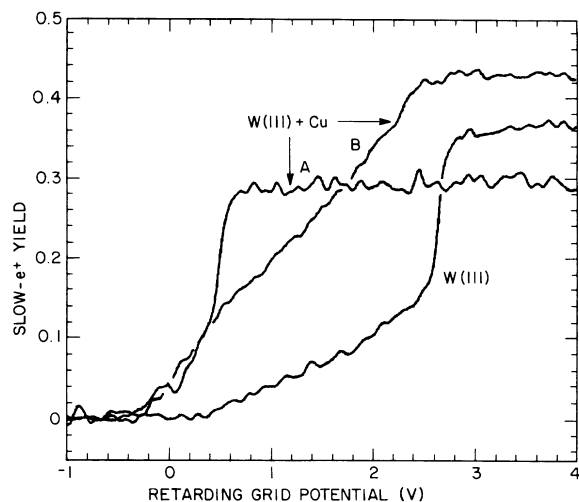


FIG. 5. Brightness enhancement obtained by evaporating epitaxial Cu(111) overlayers on the W(111) sample. The slow-positron emission after annealing (curve A) has a substantially reduced energy width. Further heating gives a spectrum, curve B, similar to W(111) + O. Electron work-function changes are apparent in this data which has not been corrected for background.

ness is uncertain and  $E_0$  is not known, hence we do not know if the beam is stopping entirely in the tungsten. The high yield does imply nearly epitaxial films but positron trapping at the interface is, in principle, possible but not likely since the yield actually increases at low coverage. This hybrid moderator should combine the stopping power of tungsten with the narrow-emission spectrum of Cu(111) and be more efficient than Cu(111) alone and three times brighter than W(111) alone.

The positron yield  $y_0$  is limited due to competing processes of bulk or surface state annihilation and Ps formation. Yields are relatively insensitive to keV variations in incident beam energy implying that bulk annihilations during diffusion from the incident beam range to the surface play a minor role in our measurements. In principle the remaining branching ratios can be measured by careful observation of the spectrum of annihilation quanta as  $3\gamma$  triplet Ps decays involve energies below photopeak events. As will be seen an accurate calibration is required because  $\gamma$ -ray scattering in the target, vacuum-chamber walls, and detector also shift photopeak events to lower energies and therefore mimic Ps formation. To minimize these difficulties we bias the target to recollect all emitted positrons so that the entire incident flux annihilates near the sample where the counting efficiency and inelastic photon scattering hopefully remain constant. To determine the fraction of incident positrons trapped in the surface state we plot counts obtained for pho-

topeak events as a function of the W(111) sample temperature in Fig. 6. The observed decline is attributed to thermal activation of triplet Ps formation from bound positron surface states<sup>9</sup> and suggests that at least 10% of positrons in the incident beam annihilate in the surface state at the lower temperatures. When activated to form triplet Ps these positrons result in a 20% increase in low  $\gamma$ -ray energy events. If counts in the low-energy range result only from triplet Ps we would estimate a low-temperature Ps fraction  $f_0=0.5$  under bias conditions where all emitted positrons are recollected. However,  $\gamma$ -ray scattering of photopeak quanta or escape of fast triplet Ps can reduce the expected change in low-energy count rate making this value of  $f_0$  an overestimate. We cannot measure the intrinsic positronium fraction  $f_0$  accurately without calibrations to correct for these possibilities but we expect that Ps formation, surface state trapping, and positron-emission branching ratios are all sizable. To estimate the surface state binding energy we represent the positronium fraction  $f$  in terms of intrinsic and activated fractions through the thermodynamic relation

$$f = f_0(1 + \alpha e^{E_A/kT})^{-1}$$

and fit the plot of photopeak counts,  $P(T)$ , to the form

$$P(T) = P(0) - (\Delta P)(1 + \beta) / (1 + \beta e^{E_A/kT}).$$

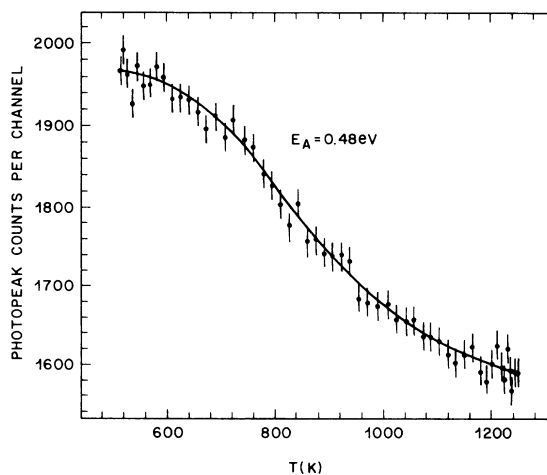


FIG. 6. Counts recorded in the photopeak  $\gamma$ -ray energy range as a function of temperature. The reduction of counts in the photopeak at higher temperatures results when positrons are desorbed as positronium through a thermally activated process. Six data points are averaged for each point plotted and for the best fit  $\chi^2/\nu \cong 36/52$ . The statistical errors indicate a  $\pm 0.04$ -V uncertainty in  $E_A$ . We estimate  $E_A = 0.48(10)$  eV to include small uncertainties in temperature measurements. The incident positron energy is 1 keV.

A good fit is obtained for  $E_A=0.48(10)$  eV which gives  $E_B=E_A-\phi_+ + \frac{1}{2}Ry=2.81(10)$  eV. It is surprising that this value is quite close to binding energies for Cu and Al even though the work functions differ tremendously.

A search for emission of the  $Ps^-$  ion<sup>21</sup> was undertaken since formation from thermalized positrons and electrons near  $E_F$  is energetically allowed. An auxiliary grid was inserted in the incident beam a few mm from the sample and biased with a large positive voltage to accelerate any negative ions formed at the target back towards the source. This should result in a Doppler shift of the  $Ps^-$  annihilation quanta which then fall in a narrow-energy range below the photopeak when monitored by a Ge (Li) detector directly behind the crystal. Our results set an upper limit of 0.1% for the  $Ps^-$  branching ratio. This method of forming  $Ps^-$  would not appear to offer a significant improvement over the beam-foil technique employed originally.

#### IV. CONCLUSIONS

W(111) should be valuable as a positron moderator. The surface can be cleaned sufficiently to give high yields by flashing to 2600°C. Carbon is the primary surface contaminant in our UHV experiments and oxygen overlayers tend to increase both

$-\phi_+$  and the gross yield. Our measured value of  $\phi_+$  is in reasonable accord with the theoretical value,  $\phi_+ = -2.8$  eV, of Nieminen and Hodges<sup>6</sup> and experimental results on uncharacterized surfaces.<sup>7</sup> Positronium fractions and surface state binding energies are comparable to other clean single crystals. Energetically allowed  $Ps^-$  formation is found to have a branching ratio below  $10^{-3}$ .

One distinctive feature of W(111) is the broad distribution of emitted positron energies. Thermal models<sup>8,25</sup> which assign kinetic energy components

$$E_{||} \approx -\phi_+ + kT, \quad E_{\perp} \approx kT$$

predict negligible energy and angular widths at room temperature where  $kT/-\phi_+ = 10^{-2}$ . Other interactions at the surface must be invoked to account for this energy width. Surface disorder is contraindicated by LEED studies and interactions with electrons is a likely alternative. For experimental situations where the beam energy resolution is important it appears to be possible to obtain epitaxial Cu(111) overlayers by *in situ* evaporation onto W(111) faces. The resulting hybrid moderator, first suggested by Lynn and Lutz,<sup>24</sup> should combine the collection efficiency of tungsten with the sharp emission characteristics of Cu(111) and may prove useful in future work.

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