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Velocity spectrum of positronium thermally desorbed from an Al(111) surface

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Time-of-flight measurements show that the spectrum of the positronium (Ps) thermally desorbed from a clean Al(111) surface is an exponentially decreasing function of the normal component of the Ps kinetic energy. The slope of the exponential obtained from samples at 443 K and 692 K gives Ps temperatures of (464±51) K and (636±64) K, in excellent agreement with the expectation of a thermally activated process. The energy spectra are consistent with the surface having a velocity-independent Ps reflection coefficient, implying there is no activation barrier. Further, the temperature dependence of the total Ps yield is consistent with the surface Ps model of Platzman and Tzoar if the reflection coefficient is zero. We confirm Lynn's observation that exposure to O_2 causes Ps to be thermally desorbed from Al at lower temperatures.

I. INTRODUCTION

It has been known for some time that positronium (Ps) atoms are formed with high probability when a metal surface is bombarded with slow positrons and that the probability of the Ps formation increases when the surface is heated.[1] Subsequent studies carried out under ultrahigh-vacuum conditions have clarified the Ps formation mechanisms as follows:

(i) Ps is formed from positrons implanted into a sample at relatively high energies which then thermalize and diffuse to the sample surface.[2]

(ii) Ps observed at low temperatures has a maximum kinetic energy equal to minus the Ps work function given by

$$-\phi_{\mathrm{Ps}} = \tfrac{1}{2}R_{\infty} - \phi_{-} - \phi_{+} \ . \tag{1}$$

For an Al(111) sample this Ps has a velocity distribution consistent with the metal being left in a one-hole excited state.[3]

(iii) The additional Ps formed at elevated temperatures is associated with a thermally activated and surface specific[4–7] mechanism.

(iv) The velocity distribution of the thermally activated Ps is consistent with the Ps being thermally desorbed from the sample.[8]

(v) At low temperatures the positrons responsible for the thermal Ps reside at the sample surface where they annihilate with a unique lifetime characteristic of a low electron density.[9]

In this paper we would like to report our new time-of-flight measurements of the velocity distribution of Ps thermally desorbed from Al(111) surfaces. From these measurements two additional conclusions follow:

(i) The thermally desorbed Ps energy spectrum from Al(111) is an exponentially decreasing function of energy and is consistent with Ps having a velocity-independent reflection coefficient. This behavior is contrary to our measurements on the Cu(111) + *S* surface.[8]

(ii) The rate coefficient deduced from the Al(111) thermal activation measurements is consistent with the Ps-like surface-state model of Platzman and Tzoar[10] if the reflection coefficient is in fact zero at thermal energies.

In the remainder of this paper we describe the experimental apparatus, present our time-of-flight Ps velocity measurements, and give the details of the arguments leading to these conclusions.

II. APPARATUS

The Ps time-of-flight apparatus[8,11] is shown in Fig. 1. A beam of slow positrons was pulsed[12] at 1 kHz to obtain 5-nsec FWHM bursts each containing ~80 positrons. The positron bursts were implanted into the sample at 2 keV, thus ensuring that most of the positrons thermalized before diffusing back to the surface where the Ps formation takes place. About 20 triplet Ps atoms formed at the sample surface after each burst. The subsequent 3γ decay of the Ps was observed by a 4 in.×8 in.×8 in. plastic scintillator counter behind a movable slit located a distance $z = 10.0 \pm 0.5$ mm upstream from the sample surface. The spatial resolution and the $z=0$ position were estab-

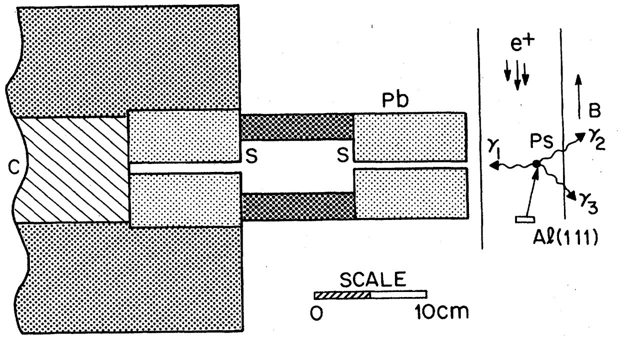

FIG. 1. Experimental arrangement for obtaining Ps velocity distributions by time-of-flight measurements. S, Pb collimator slits; *C*, 4 in.×8 in.×8 in. plastic scintillator γ-ray detector; e^+, 5 nsec burst of about 80 positrons; B, 150 G magnetic induction; γ_i, three-photon annihilation of $^3S_1$ Ps; Al(111), aluminum sample on heater stage.

lished by mapping the count rate versus z. The spatial resolution measured in this way was 1.9 mm FWHM. The 99.999% pure Al(111) sample was mounted perpendicular to the positron beam axis. It was prepared by bombardment with 1-keV Ar^{+} ions followed by annealing at 630 °C, in UHV (base pressure 3×10^{-10}Torr). Ps thermal activation measurements lead us to believe that the surface quality of our sample was comparable to that of previous samples that exhibited sharp LEED (low-energy electron diffraction) spots and less than 2% of a monolayer of O and C contamination.

The sample temperature was measured with a chromel-alumel thermocouple. Measurements of the positronium formation fraction were obtained with the positron beam energy set to 7 eV. The sample bias was -100 V so that any reemitted positrons would be eventually stopped by the sample. The annihilation γ-ray energy spectrum was measured with a 3 in.×3 in. NaI(Tl) detector on a 12-in. light pipe. The 511-keV photopeak and total count rates were converted to positronium fraction in the usual way.[2,6,13–15]

III. MEASUREMENTS

Positronium time-of-flight data obtained with the sample at two different temperatures are shown in Fig. 2. The spectra were recorded on a multichannel analyzer using a time-to-amplitude converter started by the positron accelerator pulse and stopped by the detected γ ray. The prompt peak defines $t=0$ as was established by a separate run with $z=0$ shown in the lower portion of Fig. 2.

The time-of-flight data have been converted to energy spectra shown in Fig. 3 as follows. First the background due to accidentals, taken to be the average count rate over the interval $-264<t<-44$ nsec, has been subtracted. Second, the data have been multiplied by $\exp[t/(142\text{ nsec})]$ to correct for the effect of triplet positronium annihilation. Third, the spectra have been normalized by dividing by the counting time in seconds. Finally, the data have been converted to an energy plot by multiplying by $1/t^2$ and plotting on an energy scale given by $E=m_e z^2/t^2$. The correctness of the latter transformation was verified by a Monte Carlo simulation.

The room-temperature energy spectrum shown in Fig. 3 has been scaled down by a factor 0.439 that makes the two spectra coincide over the energy range from 1 to 2.5 eV. This energy interval is where we observed the fast Ps reported in Ref. 3 in which the Ps work function for Al was measured to be $-2.62(4)$ eV. Although the fast Ps component should be independent of temperature, the scale factor differs from unity because the number of positrons diffusing to the surface is decreased at elevated temperatures by the presence of thermally activated vacancies. The change in scale also explains why the background count rates at energies above 3 eV are not the same for the two sets of data. The sharp break at $E_{\perp}=-\phi_{\text{Ps}}$ has been smeared out by the 20% spatial resolution of the slits. The low-energy portion of the figure shows an obvious excess of slow Ps for the heated sample, which, as mentioned above, is identified with the thermal desorption of the positron surface state.[16]

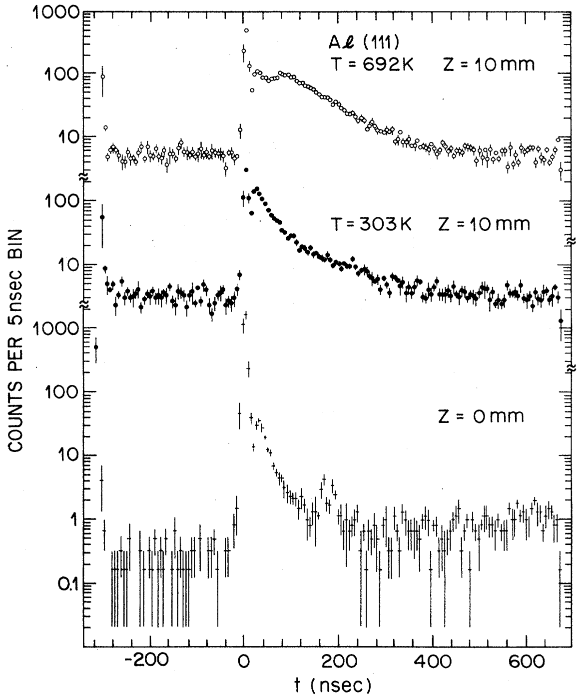

FIG. 2. Positronium time-of-flight spectra for a clean Al(111) sample at two temperatures with flight distance equal to 10 mm. Also shown is a spectrum taken with zero flight distance that establishes the $t=0$ point and shows the time resolution. The 1024 channel spectra have been added into 5-nsec bins with five 1-nsec channels collected into each bin. The error bars were obtained from the actual distribution of the averaged data. Note that this has greatly exaggerated the error bars on the sides of the prompt peaks where the slope is large. The counting times were 54 313, 32 783, and 2064 sec for the top, middle, and bottom spectra, respectively.

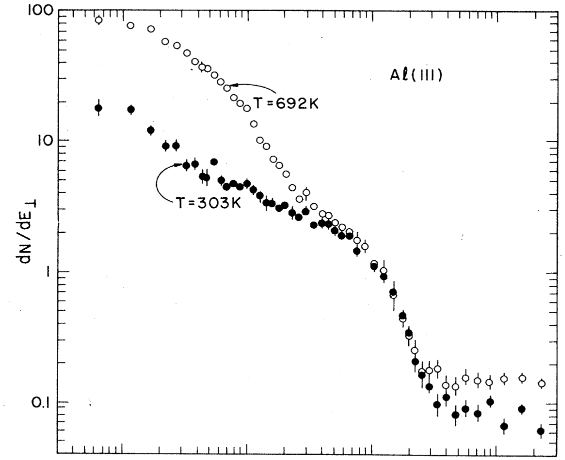

FIG. 3. Energy spectra deduced from the data of Fig. 2. The data have been regrouped into bins that are relatively uniformly spaced on the logarithmic energy scale. Above 2 eV the data points correspond to single 1-nsec channels in the original spectra.

The difference between the "hot" and "cold" spectra of Fig. 3 is displayed in the top part of Fig. 4. The solid line is a least-squares fit to the data of an exponential energy spectrum,

$$dN/dE_\perp = A\exp(-E_\perp/k_BT)\ . \tag{2}$$

The best fit parameters are $A=72$, $T=636(10)$ K, with χ^2 per degree of freedom, $\chi^2/\nu=21.67/21$. The Ps temperature has an additional systematic error of about 10% due to the 5% uncertainty in the value of z.

Figure 4 also shows a spectrum obtained with the Al sample at a lower temperature. The sample has been exposed to 75 L O_2, where 1 L$=10^{-6}$ Torr sec. The hot sample temperature was 443 K. The thermally desorbed Ps energy spectrum was again found by subtracting a room-temperature curve. In this case the hot and cold curves could be subtracted without any scale shift because there is no significant decrease in the positron diffusion constant due to thermal vacancies[17] at 443 K. The solid line is an exponential fit with parameters $A=67$, $T=464(22)$ K, and $\chi^2/\nu=26.19/17$.

As shown in Fig. 5, oxygen exposure causes the Ps fraction to increase, as reported previously by Lynn.[18] The error in the oxygen exposure could be a factor of 2 because of the large distance between the pressure gauge and the sample. Evidently, the 75-L exposure of the 443-K sample has probably made little change in the spectrum shown in Fig. 4. Spectra similar to the ones presented in Fig. 3 show that the extra Ps emitted by a room-temperature sample of Al(111) exposed to $\sim 10^3$ L O_2 also has roughly thermal energies. Unfortunately, the 213-K sample temperature used for the cold spectrum caused some absorption of contaminants over the 16-h run, and we were unable to least-squares fit the hot and cold spectra to each other in the energy interval between 0.5 and 3 eV.

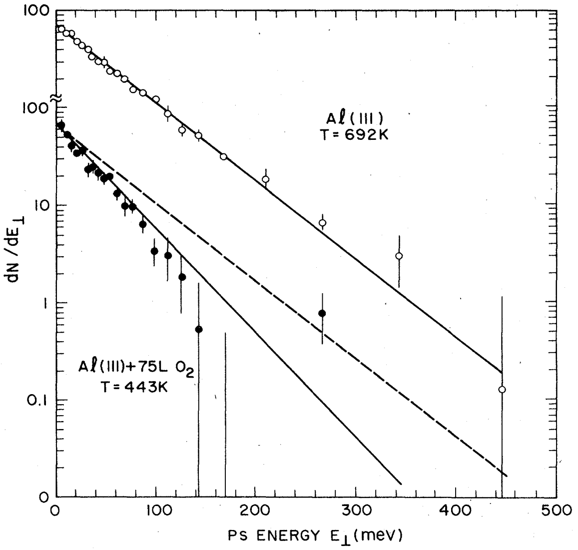

FIG. 4. Hot minus cold energy spectra for clean Al(111) and for O_2-exposed Al(111). The solid lines are least-square fits that have been used to deduce the Ps temperatures.

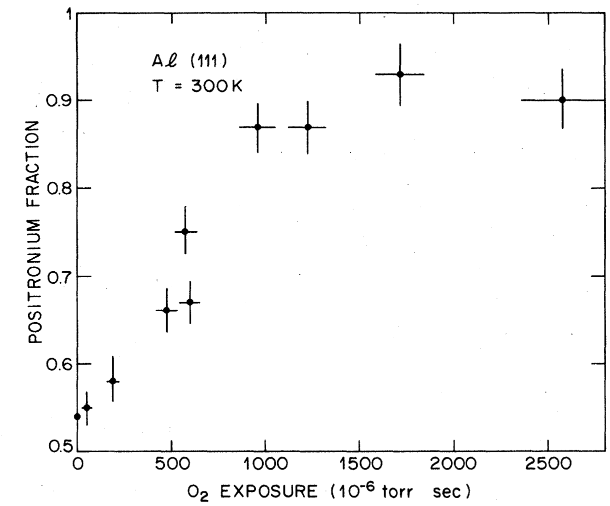

FIG. 5. Fraction of 100-eV positrons forming Ps at room temperature using an Al(111) sample exposed to various amounts of O_2 gas.

Figure 6 shows our positronium thermal activation measurements for both clean and O_2-exposed Al(111). After heating to 650 K, the heavily O_2-exposed sample seems to return to the conditions of the clean surface. The data for the clean sample show no such hysteresis, and have been fitted by an expression[5] having the temperature dependence of an Arrhenius thermally activated process,

$$f=f_0+(f_\infty-f_0)z/(\gamma+z)\ , \tag{3}$$

where $z=z_0T\exp(-E_a/k_BT)$ is the Ps thermal desorption rate, f_0 and f_∞ are the Ps formation probabilities at $T=0$ and ∞, respectively, E_a is the activation energy for Ps thermal desorption, and γ is the annihilation rate of the positron surface state. Fitting over the range $295<T<680$ K we find $f_0=0.481(3)$, $f_\infty=0.963(5)$, $z_0/\gamma=9.9\pm1.8$ K^{-1}, $E_a=0.344(7)$ eV, and $\chi^2/\nu=71.86/45$.

The systematic errors in f_0 and f_∞ are about 5% due to calibration uncertainties. Some idea of the possible systematic uncertainties in z_0/γ and E_a may be obtained by comparing the present results with the earlier measurements of Refs. 5 and 7. In these papers, the fitted curve was the same as Eq. (3) but with $z=b\exp(-E_0/k_BT)$. Using the relations

$$E_a=E_0\{1-[\ln(b/\gamma)]^{-1}\}$$

and

$$z_0=(bk/eE_0)\ln(b/\gamma)\ ,$$

we find for Al(111) from Ref. 5, $E_a=0.30(3)$ eV and $z_0/\gamma=1.9\pm1.2$ K^{-1}. From Ref. 7 we obtain $E_a=0.30(1)$ eV and $z_0/\gamma=19$ K^{-1}.

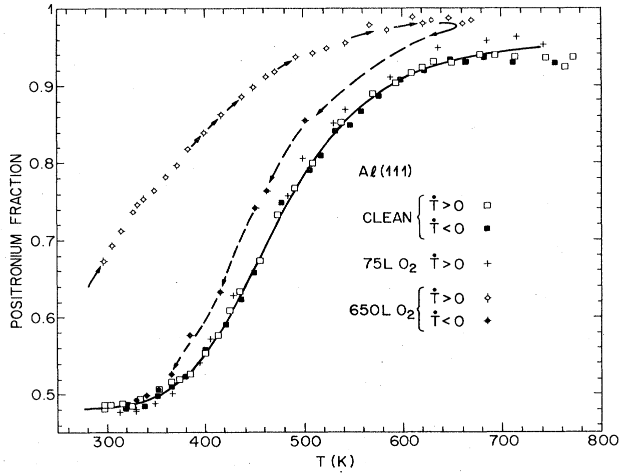

FIG. 6. Positronium fraction vs temperature for clean and O_2-exposed Al(111) surfaces. The solid line is a fitted curve for the clean Al data.

IV. DISCUSSION

The increase in Ps emission with O_2 coverage presented in Fig. 5 agrees with the measurements of Lynn[18] and is similar to the previously reported effect for submonolayer coverage of Si(100) with Cs.[19] The thermal hysteresis exhibited by the O_2-exposed Al (see Fig. 6) has also been reported by Lynn[18] and is probably connected with the conversion of chemisorbed O_2 into an Al_2O_3-like phase.[20] More recently there has been a careful study[21] of Ni(100) with alkali-metal surface contamination. This seems to indicate that increasing alkali-metal coverage slightly changes the Ps binding energy to the surface, rather than grossly affecting the positron binding energy in the image-correlation well. This would be in agreement with the Platzman-Tzoar model[10] of Ps weakly bound to the surface. In any case, it is likely that thermally desorbed Ps with a below-room-temperature energy distribution can be obtained from such surfaces.[22] Cold Ps would be very useful for atomic physics studies.[23]

Equation (3) can be derived by thermodynamic arguments similar to those leading to the Richardson-Dushman equation.[24] Imagine that we have a box containing a gas of Ps in thermal equilibrium with a population of surface positrons and that the annihilation interaction has been turned off. For a given Ps thermal desorption energy, E_a, requiring that the chemical potentials of the various components be equal allows us to deduce the density of the Ps gas and thus the rate at which Ps atoms are hitting the surface. By detailed balance, this is also the rate at which Ps atoms are leaving the surface and we arrive at the expression for z which follows Eq. (3) above. For a model in which the positrons are bound to the surface in their deep image-correlation potential well, the factor z_0 in the expression for the Ps formation rate is[24]

$$z_0=(4k_B/h)(1-\langle r\rangle)\ , \tag{4}$$

where k_B is the Boltzmann constant, h is Planck's constant, and $\langle r\rangle$ is the Ps reflection coefficient for the surface averaged over the distribution of Ps thermal velocities. Using the positron surface state annihilation rate reported[9] by Lynn *et al.*, $\gamma=1.72$ nsec^{-1}, the quantity z_0/γ becomes

$$\begin{aligned} z_0/\gamma &=(4k_B/h\gamma)(1-\langle r\rangle)\\ &=(48.37\ \mathrm{K}^{-1})(1-\langle r\rangle)\ . \end{aligned} \tag{5}$$

Comparing this to the fitted value of z_0/γ would imply that $1-\langle r\rangle=0.21(4)$. This would be in qualitative agreement with an estimate by Pendry[25] that would require $1-r$ to be proportional to the Ps energy.

In the Richardson-Dushman argument, the distribution, $dN/dE_\perp$, of the perpendicular component of the emitted Ps kinetic energy, $E_\perp$, is related to that of a gas of Ps atoms in equilibrium with the surface. By detailed balance, the energy distribution of emitted particles equals the energy distribution of particles that strike the surface and stick,

$$dN/dE_\perp=e^{-E_\perp/k_BT}(1-r)\ . \tag{6}$$

Inspection of Fig. 4 shows that $1-r$ cannot have any significant variation with energy over the range 10 meV $< E_\perp <$ 400 meV. This constancy of r seems to be at variance with Pendry's model.

It has been suggested that a Ps atom might experience an intermediate-range repulsive interaction with a surface that would cause the measured activation energy to be greater than the true Ps binding energy.[26] We may conclude from Fig. 4 that any Ps barrier height corresponding to a repulsive interaction is less than the 10-meV minimum Ps kinetic energy. These low energies also seem to rule out a "quantum tunneling" model[27] for the thermal desorption process.

A new model for the positron surface state has recently been proposed by Platzman and Tzoar[10]. In this model, Ps is weakly bound to the surface with a binding energy equal to the activation energy E_a. Compared to the surface positron model, the number of spin degrees of freedom and the mass of the two-dimensional particle are both doubled. This has the effect of reducing the value of z_0 by a factor of exactly 4, and gives instead of Eq. (5),

$$\begin{aligned} z_0/\gamma &=(k_B/h\gamma)(1-\langle r\rangle)\\ &=(12.09\ \mathrm{K}^{-1})(1-\langle r\rangle)\ . \end{aligned} \tag{7}$$

This value is consistent with Fig. 4 and the fitted value of z_0/γ if $\langle r\rangle=0$. While a perfect sticking coefficient $1-\langle r\rangle=1$ is contrary to the ideas of Ref. 25, there are arguments that would suggest that sticking of an atom at zero velocity could be possible if a surface is sufficiently compliant.[28–31] Thus our measurements can be interpreted as evidence for both the Platzman-Tzoar surface Ps model and the nonrigidity of the Ps interaction with a surface. From a microscopic point of view, the Ps emission would always be accompanied by the creation of a low-energy electron-hole pair. It is possible that if the surface electron density of states is reduced by an overlayer, the sticking coefficient might no longer be unity. Indeed, our earlier measurements on Cu(111) + S suggest that this might be the case.[32] A direct measurement of the Ps reflection coefficient for well characterized surfaces would be most interesting.

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