



THERMAL ACTIVATION MEASUREMENT OF POSITRON BINDING ENERGIES AT SURFACES

Allen P. Mills, Jr.

Bell Laboratories, Murray Hill, New Jersey 07974, U.S.A.

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The formation of positronium by low-energy positrons incident on "clean" metal surfaces is thermally activated by increasing temperature. The activation energy E_a has been measured for a number of surfaces. E_a is understood as the energy required to form positronium (binding energy $\frac{1}{2}R\gamma$) from positrons bound at the surface by an energy E_b , $E_a = E_b + \phi_- - \frac{1}{2}R\gamma$, where ϕ_- is the electron work function. Representative values of E_b derived are Al(100): 3.03(5) eV; Al(110): 2.92(4) eV; Cu(111): 2.80(5) eV.

WHEN it was discovered that positronium can be formed in vacuum by slow (~ 10 eV) positrons colliding with a solid target [1], it was also found that upon heating the targets, the fraction f of positrons yielding positronium increased to ~ 0.9 from room temperature values of ~ 0.5 . Because of the unknown surface condition of the targets, it was suggested that the increase in f could be caused by the thermal desorption of contaminants. The experiments have now been repeated under ultrahigh vacuum conditions using submonolayer-contaminated single-crystal metal target surfaces: the positronium formation also increases with temperature under these conditions and the temperature dependence is characteristic of a thermally activated process [2].

This paper offers an explanation of the observed temperature dependence in terms of a new phenomenon: the thermal desorption of positrons bound in the potential well at the target surface. Since the positrons are escaping from the surface with an electron to form positronium with ground state binding energy $\frac{1}{2}R\gamma = 6.803$ eV, the activation energy E_a for the process is related to the binding energy E_b of the positron at the surface by

$$E_a = E_b + \phi_- - \frac{1}{2}R\gamma, \quad (1)$$

where ϕ_- is the minimum energy to remove an electron from the bulk solid (the work function) and $E_b > 0$ means the positron surface state is below the vacuum level.

On the basis of Eq. 1, we can determine positron surface state binding energies E_b from the activation energy measurements reported here for the first time and from literature values of electron

work functions. The values of E_b can be derived with uncertainties of only $\sim 2\%$ and hence provide an extremely good test of our understanding of the interaction of a positron with the electron gas near a surface [3].

In a thermally activated process, a reaction energetically forbidden by a barrier E_a occurs at a rate $z = z_0 \exp(-E_a/kT)$ because of thermal fluctuations. The Boltzman factor is multiplied by a rate z_0 which will be proportional to T if our system consists of a Fermi electron gas, an ensemble of positrons free in two dimensions and an ideal gas of positronium all in thermal equilibrium [4]. In naive terms, the rate z_0 is the frequency of attempts at surmounting the barrier times a probability which depends on the details of the reaction. If the variation of the positronium formation probability, f , is thermally activated, it will have a temperature dependence

$$f = (f_0 + f_\infty \gamma^{-1} z) / (1 + \gamma^{-1} z) \quad (2)$$

where f_0 and f_∞ are the low and high temperature limits of f if $\gamma^{-1} z_0 \gg 1$ and γ is the temperature-independent rate for processes competing with the thermal activation.

The positronium fraction [5] f is obtained from the energy spectrum of the annihilation γ 's in the vicinity of the slow positron target surfaces using the apparatus and techniques described in ref. 2. Figures 1-3 show measurements of f vs T for negatively biased target surfaces of Al, Cu, and Si with various orientations and surface conditions. The positronium fraction increases from room temperature values of ~ 0.5 to ~ 0.9 at high temperatures as was observed in ref. 1. The increase in f does not seem to be associated with the desorption of surface contam-

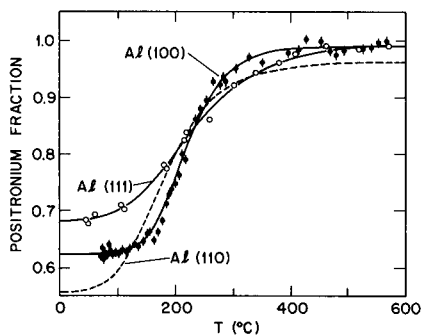


Fig. 1. Fraction of 50-70 eV positrons converted to positronium at Al target surfaces as a function of target temperature. The targets were prepared by Ar ion bombardment followed by annealing at 600°C. Sharp LEED patterns were observed and Auger spectra showed that the surface contamination by O and C was <2% of a monolayer both before and after the measurements. The "(111)" crystal face is actually cut 10° from the true (111) orientation. The LEED pattern shows evidence for a stepped surface. Only the fitted curve is shown for the Al(110) sample.

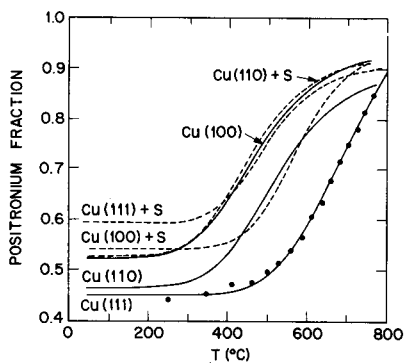


Fig. 2. Fraction of 70 eV positrons converted to positronium at Cu target surfaces as a function of target temperature. The targets were prepared by Ar ion bombardment followed by annealing at 600°C. Sharp LEED patterns were then observed and Auger spectra showed that the surface contamination by O and C was <1% of a monolayer. Sulfur was brought to the surfaces (dashed curves) by prolonged heating of the targets above 700°C. The S coverages are on the order of 1/2 monolayer. Most of the data points have been omitted for clarity and the fitted curves are shown. Each curve was obtained in 2 hr. with T increasing from 30°C. Some S was present at the end of the clean Cu runs (as a fraction of full coverage: Cu(100): S = .18; Cu(110): S = .11; Cu(111): S = .57). The amount of S present at the end of the Cu + S runs was the same as at the beginning (full coverage).

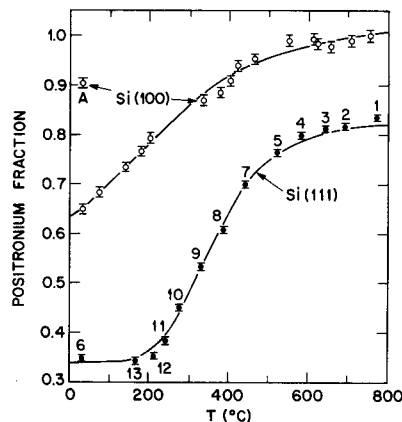


Fig. 3. Fraction of low-energy positrons [50 eV for Si(100) and 200 eV for Si(111)] converted to positronium at Si target surfaces as a function of target temperature. The targets were cleaned initially by heating to >1100°C. Auger spectra taken before and after the temperature runs revealed no O and ~2% monolayer of C. The LEED patterns were sharp 7x7 for the Si(111) and 2x1 for the Si(100). The datum A was measured when the Si(100) surface was covered with 1/2 monolayer of Cs from an evaporation source. The values of f are lower by ~.1 for Si(111) because of the higher positron incident energy. The numbers show the order in which the Si(111) data were taken.

inants. As an example we consider the Si(111) sample (Fig. 3) which was directly heated by a current and therefore had a fast thermal response time. Between the two high-temperature points numbered 5 and 7, a low-temperature measurement was made (#6). The interval between points (5×10^2 sec.) was small compared to the $>5 \times 10^3$ sec. needed to form a surface monolayer from the residual gases present ($P = 2 \times 10^{-10}$ Torr).

The curves fitted to the data in figures 1-3 have the form [6] of Eq. 2 with the best fit parameters listed in Table I. Since Eq. 2 seems to be a good representation of the data, we infer that a thermally activated process is responsible for increasing the positronium production. The activation energies E_a range from .2 eV to 1 eV and show a large variation with crystal face and surface contamination. We can thus conclude that whatever is being activated is located at or near the target surface. It is well known that thermalized positrons can be trapped in vacancies [7] which have thermal activation energies on the order of 0.5 - 1 eV. The trapping of thermalized positrons by thermally activated bulk vacancies probably does prevent implanted positrons from reaching the surface at high temperature [8,9]. However, the positronium thermal activation cannot be ascribed to bulk vacancies because E_a would not

Table 1. List of target surfaces for which the thermal activation of positronium formation has been measured.

Target	f_0^a	E_a (eV)	z_0/γ	ϕ_- (eV)	E_b (eV)
Cu(100)	.51	.56(2)	4.3(12)x10 ³	4.59(3) ^b	2.77(5)
" +S	.54	.98(3)	6.4(23)x10 ⁵	4.87(5) ^c	2.91(8)
Cu(110)	.47	.64(2)	1.1(3)x10 ⁴	4.48(3) ^b	2.97(5)
" +S	.53	.61(2)	1.7(4)x10 ⁴	4.88(5) ^d	2.54(7)
Cu(111)	.45	.85(2)	2.1(7)x10 ⁴	4.85(3) ^b	2.80(5)
" +S	.59	.76(2)	9.5(31)x10 ⁴	5.14(5) ^d	2.43(7)
Al(100)	.62	.64(2)	3.5(5)x10 ⁶	4.41(3) ^e	3.03(5)
Al(110)	.55	.40(1)	2.7(3)x10 ⁴	4.28(3) ^e	2.92(4)
Al(111)	.68	.34(3)	2.6(17)x10 ³	4.24(3) ^e	2.90(6)
Si(100)	.63	.17(3)	3.4(25)x10 ¹	4.91 ^f	2.06
Si(111)	.34	.49(5)	7.0(10)x10 ³	4.60 ^f	2.69

^a Calibration uncertainty estimated to be $\pm .10$.

^b P. O. Gartland et al., ref. 11.

^c G. G. Tibbetts et al., ref. 11.

^d Work function changes upon adding S obtained using positrons to measure contact potential differences.

^e J. K. Grepstad et al., ref. 11.

^f CRC handbook values, ref. 11.

be surface-dependent. The formation of surface vacancies is a possible mechanism, but positrons reaching surface after being implanted with energy $E < 100$ eV are highly non-thermal [8] and the trapping rate would be small.

Lacking other reasonable alternatives, we are left with the possibility that it is the positrons themselves which are being thermally activated. There is evidence that there are positron surface states [10] on metals with energy below the vacuum level. An argument can thus be made that all of the positrons implanted into a clean metal surface are not emitted as slow positrons or as positronium because there is a third energetically allowed possibility – trapping in the surface potential well. The picture which leads to Eq. 1 is that the positrons are stable in this surface well at low temperatures, but are able to form positronium by escaping from the surface with an electron if extra energy is provided by thermal fluctuations.

In Table I are presented the positron surface state binding energies E_b derived [11] from the measured values [12] of E_a using Eq. 1. The clean Cu and Al surfaces show values of E_b , 2.8 - 3.0 eV. The E_b values for Al in Table I are somewhat higher than the recent theoretical value, 2.1 eV, of Niem-

inen and Hodges [3]. Covering Cu surfaces with S tends to decrease E_b while increasing the rate z_0 compared to γ . If γ is taken to be the annihilation rate of the surface-bound positron, $\gamma \approx 10^9 \text{sec}^{-1}$, one might expect a maximum value for $\gamma^{-1}z_0$ of $\sim 10^6$ since $z_0 = 10^{15} \text{sec}^{-1}$ would be the oscillation frequency of a 3 eV bound state. Values of z_0/γ less than the maximum of $\sim 10^6$ might indicate a low density of electrons available for positronium formation [13].

The low activation energy for Si(100), .17(3) eV, suggests that if we can lower the electron work function sufficiently, the activation energy could be made zero or even negative! To test this possibility and as a check on the interpretation of the positronium thermal activation presented here, a Si(100) crystal was coated with a half monolayer of Cs (maximum coverage at 300 K). The electron work function dropped by 3.2 volts and the positronium fraction (point A in Fig. 3) rose from .65 to .9 in striking confirmation of the ideas leading to Eq. 1.

A thermal positron reaching a metal surface from within the crystal is probably very quickly (10^{-14} - 10^{-15} sec) emitted as a free particle or as positronium or is trapped in the surface well. Positrons trapped at the surface have a relatively long time ($\sim 10^{-9}$ sec) to interact with the lattice. Under the

present view, the extra positronium which forms as a result of heating the crystal should thus have an energy distribution which is nearly thermal. Furthermore, the extra positronium emitted upon coating a surface (e.g., Si(100)) with Cs should have a narrow energy distribution centered at a relatively high energy (~ 3 eV for Si(100)). Since ϕ_- can be varied easily by changing the amount of Cs, one might be able to produce a positronium beam with variable energy for scattering experiments.

The model of positronium being thermally activated from a positron surface-bound state is con-

sistent with all the available data and leads to a satisfactory picture of what happens to a thermalized positron diffusing to a surface. Experiments to test the model further by measuring the positronium velocity distributions are needed.

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- [5] The fraction f is obtained from the ratio $R \equiv (T-P)/P$ formed from the NaI(Tl) detector photopeak count rate P and the total rate T as in ref. 2. While the statistical precision of f is $\pm .01$, there are systematic uncertainties in f on the order of $\pm .1$ arising from the calibrations needed to obtain f from R . The latter uncertainties do not appreciably affect the E_a values in Table I because $f(R)$ is fairly linear and one obtains nearly the same E_a 's by fitting Eq. 2 to the calibration-free R data.
- [6] The curves were fitted assuming z_0 to be temperature independent. The T dependence of z_0 might be demonstrable with more precise data.
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- [13] More complete experiments on E_a vs surface coverage and a more detailed discussion of the results will be reported elsewhere.