Positron Reflection from the Surface Potential

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We show that thermal-positron reemission and positronium formation at clean Cu(111) and Al(110) surfaces are strongly reduced at low temperatures. This is explained by quantum-mechanical reflection of the positron wave function from the surface potential. Analysis of the data yields first estimates of the different transition rates for positrons at the surface. Information on the nature of the positron-surface interaction can be obtained. We discuss the implications of our findings to other surface emission and sticking processes.

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Positron beams are used extensively to probe surface and near-surface phenomena, e.g., disorder at or near surfaces, adsorbate and overlayer properties, and surface electron structure (for a general review, see Ref. 1). keV positrons implanted into a solid rapidly thermalize and diffuse back to the surface, where a variety of surface interaction channels become available. The main processes are (i) positron (e^+) reemission into vacuum for a negative-work-function surface,[2] (ii) positronium (Ps) formation and emission,[3] and (iii) e^+ localization into the image-charge–induced surface potential,[4] with subsequent annihilation[5] or (iv) desorption as thermal Ps.[5] However, details of the positron-surface interaction are not well understood. Surface transition rates are not known and their temperature dependences have long been subject to controversy: Elementary quantum-mechanical considerations predict a strong decrease in the transmitted e^+ current (first two primarily elastic[1] processes above) at low temperatures, due to reflection of the e^+ wave function off the surface potential.[6] Thus the surface should become fully opaque at 0 K for any abruptly changing surface potential, and e^+ and Ps yields should vanish at low temperatures. However, experiment did not support these predictions, showing only weakly temperature-dependent e^+ and Ps yields down to 30 K.[7,8] To account for this discrepancy Wilson[9] proposed that all surface processes are dominated by inelastic processes, while Neilson, Nieminen, and Szymanski[10] explained the high yields by allowing the reflected e^+ many encounters with the surface.

In this Letter we show that the elastically transmitted *thermal* e^+ flux vanishes at 0 K for a negative-e^+-work-function surface. The data are consistent with simple quantum-mechanical reflection, showing that the complicated e^+-e^- interaction can be reduced to a one-dimensional potential barrier problem. The potential height at the surface corresponds to the e^+ work function ϕ_+, which includes e^+-e^- correlation effects, the surface dipole, and the zero-point energy of the e^+ Bloch state. Furthermore, we extract first estimates of e^+ transition rates to the different interaction channels at the surface. Our data suggest a new interpretation of the Ps emission process and, more generally, give evidence on the lack of sticking of low-energy particles on cold surfaces.

Measurements of e^+ branching ratios are almost exclusively based on the determination of the backdiffusion probability. However, it has recently been demonstrated[11,12] that a significant fraction of the measured signal up to fairly high incident energies originates from e^+ which did not reach thermal equilibrium prior to escape from the sample. Thermal e^+ motion in solids can be described by the diffusion equation,[1,6] yielding the e^+ backdiffusion probability, for an incident energy E,

$$J(E)=\frac{\nu}{\nu+L_+/\tau}\int_0^\infty P(z,E)e^{-z/L_+}dz\,, \qquad (1)$$

where $\nu=\nu_{e^+}+\nu_{\rm Ps}+\nu_s$ is the total transition rate out of the bulk. The subscripts denote e^+ and Ps emission and trapping to the surface state, respectively. L_+ is the e^+ diffusion length, τ is the mean lifetime of a freely diffusing e^+ (110 ps for Cu), and $P(z,E)$ is the e^+ implantation profile.[12–14] Usually ν is assumed to be both constant and large compared to L_+/τ, i.e., possible reflection has been neglected. The problem can be reduced to one dimension, because parallel momentum is conserved in all surface processes,[6] and, on the other hand, our experimental data are averaged over lateral dimensions.[1,15] Experimental emission yields are

$$f_{e^+}(E)=\frac{\nu_{e^+}}{\nu}J(E),\quad f_{\rm Ps}(E)=\frac{\nu_{\rm Ps}+\nu_s f_d}{\nu}J(E)\,. \qquad (2)$$

The latter allows for e^+ trapped at the surface to desorb as Ps at elevated temperatures with $f_d=\lambda_d/(\lambda_d+\lambda_s)$, where λ_d and λ_s stand for the desorption and surface annihilation rates, respectively.[1] While ν_s represents a deeply inelastic process, which can be assumed to be temperature independent,[6] the elastically transmitted flux is subject to reflection. In metals Ps formation occurs in the low-electron-density region outside the surface, and thus both ν_{e^+} and $\nu_{\rm Ps}$ should be proportional to

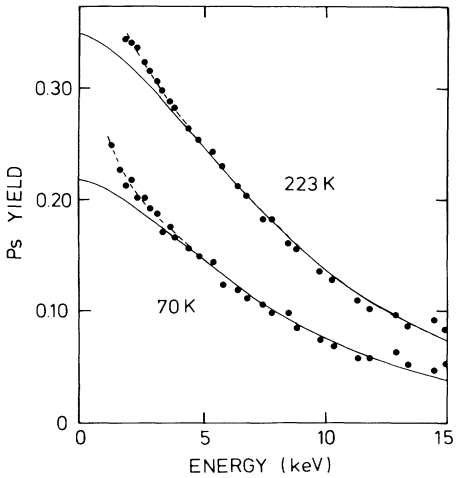

FIG. 1. Experimental Ps yields at 70 and 223 K. The solid line is a fit by Eq. (1) describing thermal-positron motion.

the transmission probability $\mathcal{T}$,

$$v_{Ps}=Pv_0\mathcal{T},\quad v_{e^+}=(1-P)v_0\mathcal{T}, \tag{3}$$

where P is the electron pickup probability outside the surface[1,6] and v_0 is a constant. Since the initial e^+ energy is thermal, $\mathcal{T}$ vanishes at 0 K.

Reemitted e^+ and Ps yields for a clean Cu(111) surface were measured as a function of incident e^+ energy at temperatures down to 24 K with a beam of 5×10^6 e^+/s (Ref. 15) under UHV conditions having a base pressure of 5×10^{-11} Torr. The (99.9999%+)-purity single crystal was cleaned with standard Ar^+ sputtering and annealing cycles and the surface was monitored with LEED and Auger-electron spectroscopy (AES). The main contaminant was carbon at <1 at.% coverage. Even at 30 K the AES peak intensities and e^+ and Ps yields remained constant over 30 min, after flash heating the surface to above room temperature, and then decreased, presumably due to hydrogen adsorption. No oxygen contamination was observed. All measurements, at each temperature, were completed within 15 min of cleaning the surface. The yields were measured with standard methods[1] by observing annihilation γ-ray spectra with a Ge detector, with a grid in front of the sample either repulsive or attractive to reemitted positrons. We also measured the shape of the reemitted e^+ energy distribution, by sweeping the grid bias through the sample voltage. Because of the finite-energy resolution and the absence of inelastic or large-angle reemission events[1] the e^+ work function ϕ_+ could only be determined to be -300 meV $<\phi_+<0$ at all temperatures below 300 K.

Figures 1 and 2 show the experimental yields[16] at 70 and 223 K. To extract the thermal-e^+ contribution two different methods were used: (i) The low-energy data were omitted until fits by Eq. (1) gave stationary values of L_+ and $\chi^2\approx1$ (Ref. 12), and (ii) the epithermal e^+ contribution was modeled with another Laplace transform with $l_+\sim20$ Å.[17] Both methods produced the same results. We also determined L_+ from annihilation line-shape measurements[1] performed for an Ar^+-sputtered and an oxidized surface.[18] All methods gave the same result for the e^+ diffusion length, $L_+=1240\times(160)[T/(300\text{ K})]^{-0.29(2)}$ Å. The implantation profile was taken to be $P(z,E)=-d\{\exp[-(z/z_0)^2]\}/dz$,[14] with $z_0=(4.5\ \mu\text{g cm}^{-2})[E/(1\text{ keV})]^{1.55}$. The corresponding fits, for the thermal yields, are shown as solid lines in the figures. The inset in Fig. 2 shows the reemitted e^+ integral energy distribution at three different temperatures for an incident e^+ energy of 3 keV.

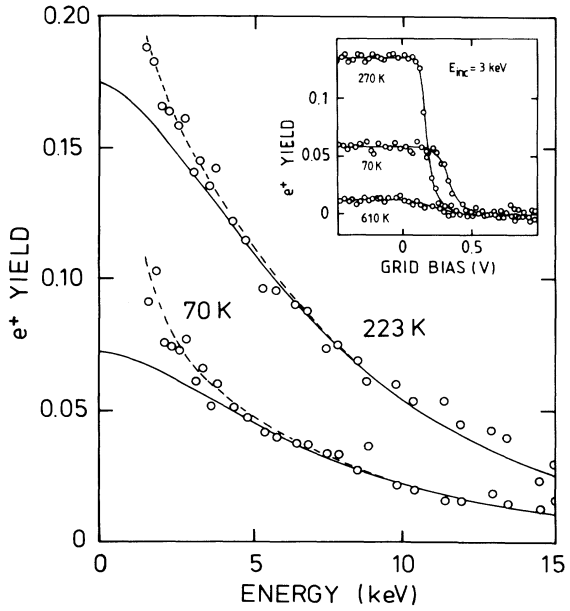

FIG. 2. Experimental e^+ yields at 70 and 223 K. The solid line is a fit by Eq. (1) describing thermal-positron motion. Inset: The reemitted energy spectrum for 3-keV incident e^+ at 70, 270, and 610 K.

Figures 1 and 2 clearly demonstrate that both yields are strongly depleted at low temperatures, while the reemitted e^+ energy distribution remains sharp, indicating an elastic escape process. The thermal yields, extrapolated to zero incident energy, are shown in Fig. 3. Both yields decrease monotonically below 300 K, vanishing at 0 K in accord with reflection from the surface. Above 300 K, where ϕ_+ is positive, $f_{Ps}(0)$ stays roughly constant, while $f_{e^+}(0)$ decreases and the reemitted e^+ energy distribution (Fig. 2, inset) becomes very broad. Finally, above 600 K (not shown), f_{Ps} exhibits the typical behavior of thermal desorption from the e^+ surface state,[1] approaching $f_{Ps}(0)=1$ at 1100 K, with $\lambda_d\propto\exp\{[-0.9(2)\text{ eV}]/k_BT\}$.[18] We have also measured f_{Ps} between 24 and 600 K for a clean Al(110) surface.[18] The overall behavior is qualitatively similar to the present Cu(111) data.

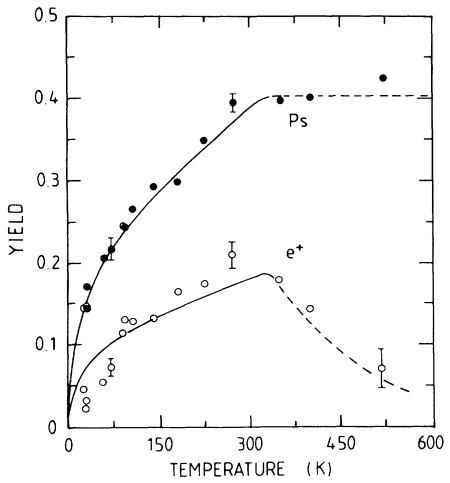

FIG. 3. Extrapolated zero-incident-energy e^+ and Ps yields as a function of temperature for Cu(111). The solid lines are fits of the Ps yield by Eqs. (1)–(4), using the values given in Table I and assuming 65% of the reemitted and returned e^+ to form Ps.

To describe[19] the temperature dependence of the branching ratios $f_{e^+}(0)$ and $f_{Ps}(0)$, $\mathcal{T}$ was calculated using the standard one-dimensional Schrödinger equation. The e^+ Bloch state inside the crystal was described as a plane wave with thermal kinetic energy $\frac{1}{2}k_BT$. Although only the perpendicular momentum component is considered, the kinetic energy in excess of the zero-point energy of the e^+ Bloch state is in fact truly small in all three dimensions. This is not the case in most surface scattering problems, where the parallel momentum remains large.[20,21] At very low perpendicular momenta the surface potential appears as an infinite step and thus reflects perfectly. To extract values of $\mathcal{T}$ vs T, the e^+ surface potential was taken to be an abrupt step of height $|\phi_+|$. The solution for $\phi_+ < 0$ yields

$$\mathcal{T} = \frac{2[k_BT(k_BT-2\phi_+)]^{1/2}}{k_BT-\phi_++[k_BT(k_BT-2\phi_+)]^{1/2}}. \quad (4)$$

The values of $\phi_+(T)$ were obtained from the Ps work-function data of Rosenberg, Howell, and Fluss[22] combined with electron work-function ϕ_- data.[23] This gives a linear $\phi_+(T) = -260$ meV $+(0.8$ meV/K$)T$. Our measured $\phi_+ + \phi_-$ data (Fig. 2, inset) agree with Ref. 22.

The solid lines in Fig. 3 are the fitted yields, calculated from Eqs. (1)–(4) below 300 K, using the three transition rates, ν_{e^+}, ν_{Ps}, and ν_s, as free parameters. The fit was initially made for the Ps yield and the e^+ yield is calculated with the same values for the parameters (Table I). A good overall agreement is seen in both cases. We have also analyzed annihilation line-shape data from clean Cu(111) and Al(110). A similar reflection model describes the data. For Cu(111) the temperature behavior in all three measurements can be modeled using the same parameter values.[18]

We have also calculated $\mathcal{T}$ for a more realistic shape[24] of the surface potential.[18] Although its absolute value varies significantly from that given by Eq. (4), the overall temperature dependence is very similar. We emphasize that our data, especially below 100 K, can only be explained if $\mathcal{T}$ vanishes at 0 K. Agreement cannot be reached by simply varying the work function or the shape of the surface potential. However, the use of a more realistic potential reverses the ϕ_+ dependence of $\mathcal{T}$ in comparison with that obtained from Eq. (4). This explains some of the findings of Gullikson, Mills, and Murray[25] who observed an increase in the e^+ yield with $|\phi_+|$ at room temperature.[18] As more accurate transmission measurements become available, fits to the temperature behavior of $\mathcal{T}$ can be used to obtain quantitative information on the shape of the surface potential.

Our results are compatible with elementary predictions of particle transmission through a potential barrier, and the elastic current through the surface vanishes at 0 K. More surprisingly, Ps formation is governed by the same wave-mechanical reflection, indicating a two-step process, in which the electron pickup probability P outside the surface, after elastic e^+ transmission, has no apparent temperature dependence. Information has also been obtained, for the first time, on the absolute values and temperature dependences of the various transition rates at the surface. Both the present data and annihilation line-shape measurements[18] show that the surface trapping rate is $\nu_s \approx 10^5$ ms^{-1} with practically no temperature dependence. Our findings are direct observations of quantum-mechanical reflection, where we have utilized the fact that positrons have thermalized, in all three dimensions, down to at least 24 K.[26] Inappropriate separation of the thermal and epithermal contributions from the measured data is one of the reasons explaining the failure of the early experiments[7,8] to observe e^+ reflection.[18]

TABLE I. Values of the parameters used to fit the experimental data for Cu(111) and calculated transition rates at 30 and 300 K. For definitions see the text.

ν_s (10^5 ms^{-1})	P	ν_0/ν_s	ν_{e^+}/ν_s 30 K	ν_{e^+}/ν_s 300 K	ν_{Ps}/ν_s 30 K	ν_{Ps}/ν_s 300 K
1.0(7)	0.60(5)	0.89(2)	0.09(1)	0.22(1)	0.13(1)	0.33(1)

Reflection will also affect other experimental surface studies: E.g., the value of the sticking coefficient for low-energy helium scattering at low temperatures is a long-standing problem.[20] Our observations suggest that a low-energy particle approaching a cold surface has a zero sticking probability. Also, fine structures in very-low-energy e^- and e^+ diffraction[21] have been argued to arise from reflection off the surface potential, but the subject is still under debate. The suggested two-step nature of Ps formation and emission process may also give new insight into discussion on other surface emission problems (e.g., for photoemission, see Ref. 27).

In conclusion, our experimental data from clean Cu(111) and Al(110) surfaces allow us to say the following: (i) Thermal-positron elastic transmission from the bulk is strongly reduced at low T; (ii) the data can be described by quantum-mechanical reflection of the positron wave function from the surface potential; (iii) first estimates of the different transition rates of positrons at the surface and their temperature dependences are obtained; (iv) positron and positronium emission can be described by the same transmission model; (v) we suggest that positronium emission is a two-step process with T-independent electron pickup probability; and (vi) our data support vanishing sticking of low-energy particles at cold surfaces.

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[1]P. J. Schultz and K. G. Lynn, Rev. Mod. Phys. **60**, 701 (1988).

[2]A. P. Mills, Jr., P. M. Platzman, and B. L. Brown, Phys. Rev. Lett. **41**, 1076 (1978).

[3]K. F. Canter, A. P. Mills, Jr., and S. Berko, Phys. Rev. Lett. **33**, 7 (1974).

[4]C. H. Hodges and M. J. Stott, Solid State Commun. **12**, 1153 (1973).

[5]K. G. Lynn, Phys. Rev. Lett. **43**, 391 (1979).

[6]R. M. Nieminen and J. Oliva, Phys. Rev. B **22**, 2226 (1980).

[7]K. G. Lynn, P. J. Schultz, and I. K. MacKenzie, Solid State Commun. **38**, 473 (1981).

[8]P. J. Schultz and K. G. Lynn, Phys. Rev. B **26**, 2390 (1982).

[9]R. J. Wilson, Phys. Rev. B **27**, 6074 (1983).

[10]D. Neilson, R. M. Nieminen, and J. Szymanski, Phys. Rev. B **33**, 1567 (1986).

[11]R. H. Howell, I. J. Rosenberg, and M. J. Fluss, Phys. Rev. B **34**, 3069 (1986).

[12]H. Huomo, A. Vehanen, M. D. Bentzon, and P. Hautojärvi, Phys. Rev. B **35**, 8252 (1987).

[13]S. Valkealahti and R. M. Nieminen, Appl. Phys. A **35**, 51 (1984).

[14]A. Vehanen, K. Saarinen, P. Hautojärvi, and H. Huomo, Phys. Rev. B **35**, 4606 (1987).

[15]J. Lahtinen, A. Vehanen, H. Huomo, J. Mäkinen, P. Huttunen, K. Rytsölä, M. Bentzon, and P. Hautojärvi, Nucl. Instrum. Methods Phys. Res., Sect. B **17**, 73 (1986).

[16]Actually the measured Ps fraction data were obtained with a repulsive grid. In the subsequent data analysis we assumed that 65% of all reemitted and returned positrons formed Ps.

[17]D. T. Britton and P. C. Rice-Evans, Philos. Mag. Lett. **57**, 165 (1988).

[18]A more detailed report will be published elsewhere.

[19]Note that $J(0)=\nu^*(\nu+L_+/\tau)^{-1}$.

[20]V. U. Nayak, D. O. Edwards, and N. Masuhara, Phys. Rev. Lett. **50**, 990 (1983); M. Sinvani, M. W. Cole, and D. L. Goodstein, Phys. Rev. Lett. **51**, 188 (1983).

[21]R. O. Jones and P. J. Jennings, Surf. Sci. Rep. **9**, 165 (1988).

[22]I. J. Rosenberg, R. H. Howell, and M. J. Fluss, Phys. Rev. B **35**, 2083 (1987).

[23]J. Hölzl and F. K. Schulte, in *Solid Surface Physics,* Springer Tracts in Modern Physics Vol. 85 (Springer-Verlag, Berlin, 1979), p. 78.

[24]P. J. Jennings and D. Neilson, Solid State Commun. **65**, 649 (1988); M. Puska and R. M. Nieminen, Phys. Scr. T **4**, 79 (1983).

[25]E. M. Gullikson, A. P. Mills, Jr., and C. A. Murray, Phys. Rev. B **38**, 1705 (1988).

[26]P. Kubica and A. T. Stewart, Phys. Rev. Lett. **34**, 852 (1975).

[27]N. V. Smith and F. J. Himpsel, in *Handbook on Synchrotron Radiation,* edited by E.-E. Koch (North-Holland, Amsterdam, 1983).