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Thermodynamics of positronium thermal desorption from surfaces

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A formula equivalent to the Richardson-Dushman equation for thermionic emission is derived for positronium emission from metal surfaces. Data on clean copper surfaces agree with the thermodynamic equation if one takes an effective reflection coefficient of thermal Ps incident on the copper surfaces to be $\simeq 0.9$. For submonolayer converage of sulfur on copper, the positronium emission exceeds the simple thermodynamic limit, and the implications of this result are explored.

The properties of positron surfaces states[1] have been calculated by Hodges and Stott[2] and by Nieminen and Manninen,[3] who noted the large change in annihilation characteristics in neutron irradiated molybdinum.[4] Positron-lifetime and angular-correlation measurements in metal powders have also been explained by invoking the existence of surface states.[5] More recently, experiments using slow (~ 10 eV) positrons incident on well-characterized single-crystal metal surfaces have provided more direct evidence of positron surface states. In these experiments, the fraction f of the incident positrons forming positronium has a temperature dependence[6] characteristic of a thermally activated process.[7,8] This phenomenon is explained by a model in which positrons bound in their "image" potential well at the surface, are thermally desorbed as positronium when sufficient energy is supplied by thermal fluctuations. The thermal activation measurements can be analyzed using thermodynamic arguments to obtain the positron surface-state binding energies E_b, and estimates of the positronium formation rate constants.

The scenario[8] for the trapping of positrons in surface states is shown schematically in Fig. 1, and can be outlined as follows. Slow positrons penetrate into a metal and quickly lose their energy by either plasmon or phonon scattering. While some of the positrons annihilate with electrons in the bulk crystal, most of them diffuse to the surface and encounter a surface dipole layer that may give the positron a negative work function.[9] As the positron leaves the surface it sees an effective potential well due to a modified image potential at large distances from the metal surface and electron correlation at small distances. Multiple scattering at the well boundaries may occur, and either nonthermal free positrons or positronium (Ps) will emerge or else the positron will undergo inelastic collisions and fall into the surface well. Once in the well the positron can either annihilate (principally into two γ rays) or else escape from the surface as free positronium if sufficient energy is available from thermal fluctuations.

The fraction f of Ps produced from an incident positron is typically 0.5 at room temperature and increases to ~ 0.9 at elevated temperatures. The temperature dependence of f fits an activation curve that can be described by a Ps formation rate of the form $z = z_0 \exp(-E_a/kT)$ where the activation energy E_a is dictated by energy balance

$$E_a = E_b + \Phi_- - \tfrac{1}{2} R_\infty \ , \tag{1}$$

where Φ_- is the bulk electron work function, $\frac{1}{2}R_\infty = 6.8$ eV accounts for the ground-state binding energy of Ps, and $E_b > 0$ is the binding energy of the positron at the surface. Suppose we let f_0 denote the (nonthermal) fraction of positrons that directly form positronium (low-temperature limit) and f_s be the fraction that becomes trapped in the surface well. Then the fraction f_t of positrons that are thermally desorbed from the surface as free positronium will be

$$f_t = \frac{z f_s}{\gamma + z} = \frac{z_0 e^{-E_a/kT} f_s}{\gamma + z_0 e^{-E_a/kT}} \ , \tag{2}$$

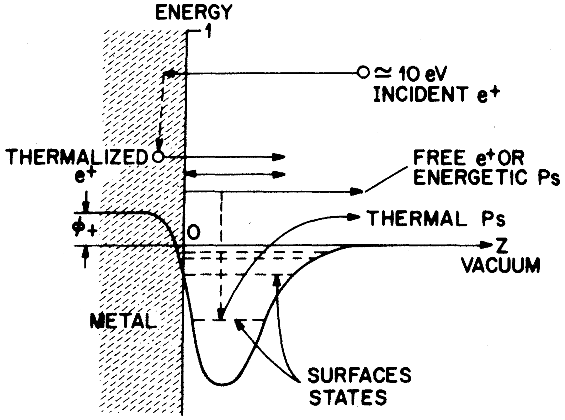

FIG. 1. Schematic representation of some of the processes that occur when slow positrons are near a surface. Other processes not shown include Bragg scattering of the positron and 2γ annihilation in the bulk or on the surface.

where γ is the 2γ annihilation rate of the positron surface state. The fraction f_t can be related to the experimentally determined high-temperature limit $f_\infty = f_0 + f_t$ at $T \to \infty$. If we assume that $\gamma << z_0$, and f_s is only a weak function of temperature, we find that the positronium formation fraction f is given by

$$f = f_0 + f_t = \frac{f_0 + (z/\gamma) f_\infty}{1 + (z/\gamma)} \quad . \tag{3}$$

In Ref. 8, values of E_a and z_0 have been fitted to activation data for various surfaces of Cu, Al, and Si, assuming that z_0 was temperature independent.

The preexponential factor z_0 may be qualitatively explained as an attempt rate having something to do with the positron's thermal velocity $v \cong 10^7 \text{ cm sec}^{-1}$ and the dimensions of the "image" potential well $a \cong 10^{-8}$ cm. Thus $z_0 \cong v/a \cong 10^{15} \text{ sec}^{-1}$. A complete quantitative account of positronium thermal desorption must include details of the electrons spatial distribution near the physical surface of the metal and energy distribution near the Fermi surface, and the dynamic correlation of the electron cloud about the positron. However, standard statistical arguments can recover the form of Eq. (1) and provide interesting upper limits to z_0.

Our treatment is very similar to the derivation of the Richardson-Dushman equation,[10] for ordinary thermionic electron emission except that we consider a reaction involving three species

$$e^+ + e^- \leftrightarrow \text{Ps} \tag{4}$$

in thermal equilibrium. In our model, the positrons are confined to the surface, the electrons may be in both surface and bulk states, and the positronium forms a classical ideal gas in the vacuum. The condition for chemical equilibrium is the equality of the chemical potentials,

$$\mu_{e^+} + \mu_{e^-} = \mu_{\text{Ps}} \quad . \tag{5}$$

The chemical potential μ_{Ps} can be related to the single particle partition function Z_{Ps} via

$$\mu_{\text{Ps}} = -kT \ln \frac{Z_{\text{Ps}}}{N_{\text{Ps}}} \quad , \tag{6}$$

where N_{Ps} it the total number of positronium atoms in the system, and

$$\begin{aligned} Z_{\text{Ps}} &= \sum_i e^{-E_i/kT} \\ &= 4 \int \frac{d^3p\, d^3x}{h^3} \exp\left[-\left(\frac{P^2}{2M_{\text{Ps}}} - \tfrac{1}{2} R_\infty \right) \Big/ kT \right] \quad , \end{aligned} \tag{7}$$

includes a sum over all accessible states i. The sum has been converted into an integral over phase space cells $(dp_1 \cdots dp_f dx_1 \cdots dx_f)/hf$, where f is the number of generalized coordinates. The factor of 4 accounts for the spin degeneracy of positronium. The integral yields the relation for the density n_{Ps} of positronium

$$\begin{aligned} n_{\text{Ps}} &= \frac{N_{\text{Ps}}}{L^3} \\ &= e^{\mu_{\text{Ps}}/kT} 4 \left(\frac{2\pi M_{\text{Ps}} kT}{h^2} \right)^{3/2} \exp(\tfrac{1}{2} R_\infty / kT) \quad . \end{aligned} \tag{8}$$

The flux of incident Ps that are not reflected from the surface per cm^2 per sec is

$$F = n_{\text{Ps}} \left\langle \frac{v(1-r)}{2} \right\rangle_z = n_{\text{Ps}} \left(\frac{kT}{2\pi M_{\text{PS}}} \right)^{1/2} (1 - \tilde{r}) \quad , \tag{9}$$

where $r = r(v_z)$ is the reflection coefficient, F is the flux, and $\tilde{r}$ is the velocity averaged reflection coefficient. By detailed balance, this flux must equal the number of Ps atoms thermally activated from the surface. Equations (5), (8), and (9) reduce the problem to finding the chemical potentials of μ_{e^+} and μ_{e^-}.

Suppose we consider the case where the electrons are bulk conduction electrons and the bound positrons are a classical gas in two dimensions. Excitation of the surface bound positrons corresponding to the degree of freedom perpendicular to the surface is assumed to require energies much higher than the relevant thermal energies. Then $\mu_{e^-} = -\Phi_-$ where Φ_- is the usual electron work function, and

$$\mu_{e^+} = -kT \ln \left(\frac{4\pi mkT}{n_{e^+} h^2} \right) - E_b \quad , \tag{10}$$

where n_{e^+} is the surface density of e^+. Equation (10) has been calculated in the same way as Eqs. (6) and (7) except the phase space dimension $f = 2$ and the spin degeneracy is 2. Combining Eqs. (5)–(10) yields the simple result

$$z = \frac{4kT}{h} e^{-E_a/kT} (1 - \tilde{r}) \quad , \tag{11}$$

where $E_a = E_b + \Phi_- - 1/R_\infty$. Thus, we recover Eq. (1) with z_0 given in terms of fundamental physical constants.

Of course, one can also calculate z_0 for other positron configurations. For example, if we consider the case where the positrons are trapped locally at defect sites on the surface, the partition function is

$$z_{\text{defect}} = \sum_i e^{-E_i/kT} = N_T = \rho_D L^2 \quad , \tag{12}$$

where N_T is the total number of defect states, ρ_D is the surface defect density, and L^2 is the area of crystal surface. The result for this model gives a prefactor

$$z'_{\rm defect}=\frac{16\pi m(kT)^2}{\rho_D h^3}\ . \qquad (13)$$

If the average distance between defects is on the order of 20 Å, $z_{\rm defect}$ is an order of magnitude larger than z for a 2D gas at 700 K. The point-defect model and the 2D perfect gas represent two extremes of an actual physical system, and a natural question is whether the positrons on a particular surface are in localized or extended states. However, by looking at z_0 as a function of annealed or damaged surfaces, significant changes in z_0 would point to more localized positron states.

Equation (11) cannot be directly compared to experiment since the thermal activation data measure z_0/γ. Nieminen and Manninen[3] have calculated γ for positron surfaces states in aluminum to be $\sim 2.7\times 10^9$ sec^{-1}. Bhattacharyya and Singwi[11] considered the positron annihilation rate in bulk metal as a function of electron density, and find that the rate for low electron density approaches 2×10^9 sec^{-1}, the spin-averaged annihilation rate of free positronium. Thus, it would seen unlikely that γ could be significantly smaller than 2×10^9 sec^{-1}.

The prefactor in Eq. (11) has additional temperature dependence in the reflection coefficient. The velocity dependence of the reflection coefficient of positronium with thermal velocities incident on a Cu(111) surface has been measured by Mills and Pfeiffer.[12] For velocities less than 3×10^7 cm/sec they find that the transmission coefficient

$$1-r\sim 1+(v_z/v_0)^2\sim 1+({\rm const})T\ , \qquad (14)$$

where $v_0=8.7(1.3)\times 10^6$ cm/sec and v_z is the velocity of Ps normal to the surface. The magnitude of $1-r$ has not yet been established, but the data of Ref. 12 suggest that it is probably in the range of 0.05 to 0.5. If one neglects the small nonvanishing sticking coefficient at $v_z=0$ in Eq. (14) and averages over all v_z, one can easily show that

$$(1-\bar r)=\frac{\pi}{4}\left[\frac{\bar v}{v_D}\right]^2\propto T\ .$$

Pendry[13] has calculated $1-r$ for electrons incident on Cu(001) and finds a similar value for the magnitude of $1-\bar r$, but predicts a $\sqrt{T}$ dependence.

We have made a least squares fit[14] to the data of Ref. 8 using

$$z=z'_0Te^{-E_a/kT}\ , \qquad (15)$$

so that z'_0 can be compared to the thermodynamic value of the prefactor given by

$$z_{\rm th}=\left[\frac{4k}{h}\right]\frac{1}{\gamma}(1-\bar r)=\frac{8.33\times 10^{12}}{\gamma}\ ({\rm sec}^{-1})(1-\bar r)\ . \qquad (16)$$

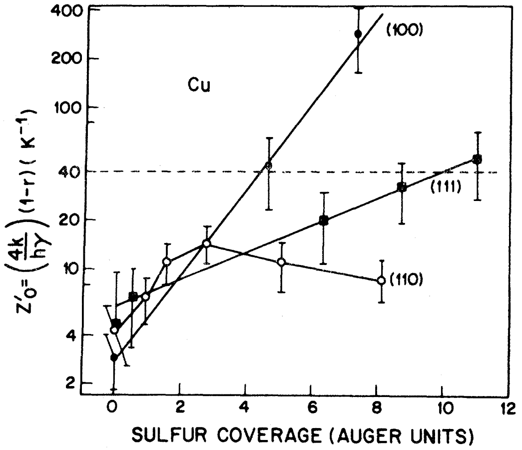

FIG. 2. Exponential prefactor z_0 as a function of sulfur coverage. A saturated sulfur monolayer corresponds to 14 Auger units. The thermodynamic upper limit for our model given by the dotted line corresponds to $\gamma=2\times 10^9$ sec^{-1} and $1-r=1$.

In Fig. 2 the fitting parameter z'_0 is plotted as a function of sulfur coverge, N_s, on various copper surfaces. For likely values of $\gamma\cong 2\times 10^9$ sec^{-1} and $1-r\cong 0.1$, Eq. (14) gives a value for $z_{\rm th}=z'_0$ found for clean Cu surfaces. However, for increased sulfur coverage on Cu(100) and Cu(111), z'_0 is seen to increase beyond the "thermodynamic limit" given by Eq. (14) even if we let $1-r=1$ for $\gamma=2\times 10^9$ sec^{-1}. We also include in Fig. 3 a plot of E_a as a function of N_s for the copper surfaces.

In contrast to Pendry,[13] we do not believe that a large experimental z_0/γ can be interpreted as an upper limit on the size of γ since one is led to unphysically small values of γ for several surfaces. In-

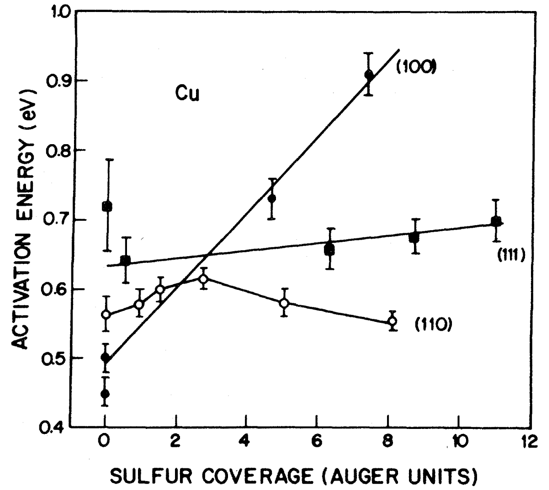

FIG. 3. Activation energy as a function of sulfur coverage for various copper surfaces.

stead, we feel that the probable explanation for the anonomously large values of z_0' is that for the contaminated surfaces E_a is temperature dependent. A negative dE_a/dT will add a factor to Eq. (15)

$$z_0' \to z_0' \exp(|dE_a/dT|/k) \ . \tag{17}$$

This situation is completely analogous to that of ordinary thermionic emission, where a negative temperature dependence of the electron work function is the usual culprit when the measured emission constant A is larger than the Richardson value[15] $A_0 = 4\pi m K^2 e/h^3 = 120\ \mathrm{A/cm^2\,deg^2}$. (Early in the history of thermionic emission values of A several orders of magnitude higher the A_0 have been reported for metal surfaces contaminated with adsorbates.)

Suppose we take the large value of z_0' in Fig. 2 as evidence for a significant negative

$$\frac{\partial E_a}{\partial T} = \frac{\partial E_b}{\partial T} + \frac{\partial \Phi_-}{\partial T} < 0 \ . \tag{18}$$

If we assume that the temperature dependence of E_b is due to the dipole layer change, and in particular to a change in the ϕ_+ of the effective potential shown in Fig. 1,

$$\frac{\partial E_b}{\partial T} = \frac{\partial E_b}{\partial \phi_+}\frac{\partial \phi_+}{\partial T} = -0.75\frac{\partial \phi_-}{\partial T} \ , \tag{19}$$

where $\partial E_b/\partial\phi_+ = -0.75$ is estimated by modeling the surface potential of the positron as an uneven square well with dimensions chosen to give $E_b = 3.4$ eV as calculated by Nieminen and Hodges.[9] Combining Eqs. (18) and (19) gives

$$\frac{\partial E_a}{\partial T} = 0.25\frac{\partial \phi_-}{\partial T} \ . \tag{20}$$

Using the measured value of $\partial\phi_-/\partial T = -(9+1) \times 10^{-4}\ \mathrm{eV}/k$ for Cu(111) plus full coverage S, Eqs. (20) and (17) requires that the fitted experimental parameter z_0' for Cu(111) + S to be larger than z_0' for clean Cu(111) by a factor of

$$\frac{\exp\left[0.25\left(\frac{\partial\phi_-}{\partial kT}\right)\mathrm{Cu+S}\right]}{\exp\left[0.25\left(\frac{\partial\phi_-}{\partial kT}\right)\text{clean Cu}\right]} \simeq \frac{14.4}{1.3} = 11 \ .$$

This estimate is in agreement with our measured increase of a factor of ~ 10 at the highest coverage on Cu(111) + S in Fig. 2, and is somewhat fortuitous given that the uneven square-well approximation for the positron's potential energy outside the surface is clearly crude. Also, E_b may possibly have additional temperature dependence neglected in Eq. (20). One speculation is that the depth of the positron potential well also changes with temperature due to changes in the correlation energy the cloud of electrons surrounding the positron. The temperature and work-function dependence of E_b could be tested by experiments using a laser to measure the excited state spectrum of surface bound positrons. We have no *in situ* measurements of $\partial\phi_-/\partial T$ for the other faces of copper and so cannot make any direct quantitative comparisons with the data for z_0' on these facts.

To summarize, the details of the thermodynamic analysis of Ps thermionic emission are given and compared with data on copper surfaces. Clean copper surfaces give results that are consistent with an average reflection coefficient of ~ 0.9. Sulfur chemisorbed on copper surfaces changes the activation energy E_a and the prefactor z_0' by modifying the dipole layer at the metal boundary. The additional dipole layer changes the electron work function ϕ_- by measured amounts, and the change in E_a as a function of sulfur coverage is partially understood in a crude model of a simple 1D "image" potential for the positron. Quantitative agreement with the measured values of z_0' using a two-dimensional free positron gas is obtained for Cu(111) + S when measured temperature dependence in ϕ_- is taken into account.

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[14] The data were also fitted to rates of the form $z = z_0'' T^{\alpha} e^{-E_a/kT}$, where α is an integer between -1 and $+4$, but the data are not precise enough to determine α. On the other hand, if α is known, it is easy to show that

$$E_a(\alpha) = E_a(0)[1 - \alpha/\ln(z_0''/\gamma)] \ .$$

The temperature dependence of z_0 is difficult to extract from the experimental data because there is no infinite source of positrons on our surfaces and the Ps emission saturates at the relatively low temperature of ~ 600 °C. In ordinary thermionic emission, there is no shortage of electrons, and one can measure electron emission over a wide range of temperature.

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