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# Positron Detrapping from Defects: A Thermodynamic Approach

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**Abstract.** The rate of positron detrapping in thermal equilibrium from lattice defects has been calculated by relating it to the specific trapping rate. The results for vacancies, dislocations and surfaces each show a different temperature dependence for the escape rate. For vacancies a measure of the importance of the detrapping can be obtained from the ratio of the vacancy formation energy to the positron binding energy in the defect. The positronium desorption rate from a surface is also calculated and agreement with experimental results is found.

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The detrapping of positrons ($e^+$) from lattice defects can affect experimental results in three different ways. First, thermally activated detrapping may be seen directly as a change in the annihilation parameters, as is most clearly observed in the emission of positronium (Ps) from a metallic surface [1–3]. Secondly, strong trapping into one kind of a trap prevents the positron from trapping into any other defect. If the binding energy in the primary traps is small ("shallow traps") and if the annihilation characteristics in them differ only slightly from those in the bulk material, thermally activated detrapping from these defects increases the relative importance of trapping into other (deeper) defect states. This is experimentally seen as an apparent strong temperature dependent trapping rate into those defects, where the annihilation characteristics are clearly different from those of the bulk [4]. Finally, the trapped state from which the detrapping takes place can act as a precursor state to a deeper trap. In this case the detrapping decreases drastically the trapping rate into these deeper traps. An example of this is the model studied by Smedskjaer et al. [5], where the dilatation field of a dislocation forms an extended defect with a small positron binding energy and provides an effective trapping channel to jogs or other point defects in the vicinity of the dislocation line.

Experimental evidence for detrapping seems to be unquestionable only in the case of thermal desorption of Ps from a positron surface state [1–3]. Maier et al. [6] have explained the anomalous temperature dependence of Doppler broadening of the $2\gamma$ annihilation line of Ta by direct detrapping of positrons from monovacancies. Similar measurements have also been carried out for other refractory metals [7]. However, this interpretation has not been accepted by Gupta and Siegel [8] who estimated the positron-vacancy binding energies to be too high to allow any substantial detrapping. Smedskjaer et al. [5, 9, 10] have explained low-temperature anomalies found in lifetime spectra, for example, in Cd and Au in terms of detrapping from dislocations, but there the temperature dependence of the trapping process (perhaps diffusion limited) is not completely ruled out as another explanation. Similarly, the apparent strong temperature dependence of positron trapping into voids in Mo has been explained by detrapping from some other shallow traps by Schultz et al. [4], whereas Nieminen et al. [11] were able to explain related behaviour for voids in Al solely by temperature dependent trapping

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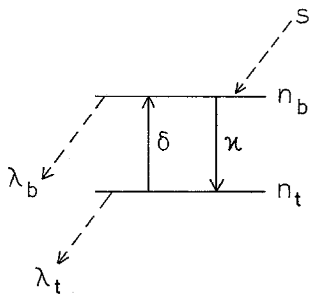

Fig. 1. Two state trapping model considered in this paper. $n_b$ and $n_t$ are the numbers of positrons in the bulk and in the trap, respectively. $S$ is the rate of positrons entering the sample, $\kappa$ is the trapping rate, $\delta$ the trapping rate, and $\lambda_b$ and $\lambda_t$ are the two annihilation rates

and diffusion rates. Note, however, that the voids in the latter study were much larger in size than those studied by Schultz et al. [4].

Efforts to estimate detrapping rates theoretically have concentrated on vacancies. The chemical rate theory [12] leads to an exponential temperature dependence of the detrapping rate, $\delta = \delta_0(T)\exp(-E_b/k_BT)$ where $E_b$ is the positron-vacancy binding energy. The rate theory for unimolecular reactions [12], as used by Goland and Hall [13], and Frank and Seeger [14], gives the prefactor $\delta_0 \propto T$. Doyama and Hasiguti [15] have estimated $\delta_0$ from the oscillation frequency of a localized positron moving with thermal velocity, which leads to $\delta_0 \propto T^{1/2}$. On the other hand, Tam and Siegel [16] used the root-mean-square velocity estimated from the kinetic energy of the localized positron to estimate the vibration frequency. This gives a temperature independent prefactor $\delta_0$. Kuribayashi and Doyama [17], and Tam and Siegel [16] have also considered the possibility of detrapping due to vacancy migration.

In this paper we use a thermodynamic approach, similar to the chemical rate theory in principle, in a more careful study of detrapping from vacancies, dislocations and surfaces. In Sect. 1 we define the assumptions made in the trapping models and give the equations showing how detrapping affects the measured annihilation parameters. Formulae for the detrapping rate from different defects are derived in Sect. 2. These should prove useful in detailed analysis of accurate experimental data.

The approximations in and limitations of the model are also investigated. The results are discussed in Sect. 3. We show that for vacancies the importance of detrapping depends only on the vacancy formation and the positron binding energies and, within the model, is independent of the specific trapping or detrapping mechanism. In this section it is also shown that the same ideas can directly be applied also for Ps desorption from surfaces, where experimental results are rapidly accruing.

## 1. Trapping Model

Figure 1 shows the diagram for the conventional two state trapping model. In equilibrium the positrons are entering the sample at a rate $S$. We make the usual assumption [18, 19] that positrons are thermalized very rapidly (thermalization time $\ll$ mean lifetime) and that immediately after thermalization the positron is in the bulk state. We further assume that only a single lifetime (or momentum parameter) is associated both with the trapped state and with the bulk state, whereas we allow for the possibility of several energy states inside the trap. Solving the rate equation for this system [18], or studying the steady state condition [5], the mean lifetime of the positron can be written as

$$\tau_M = I_1\tau_1 + I_2\tau_2 = \frac{\lambda_t + \kappa + \delta}{\lambda_t\lambda_b + \lambda_t\kappa + \lambda_b\delta}, \tag{1}$$

where $I_i$ and $\tau_i$ are the intensities and lifetime components of the spectrum, $\lambda_b$ and $\lambda_t$ are the annihilation rates in the bulk and in the defect, $\kappa$ is the trapping rate and $\delta$ the detrapping rate. Similarly defining a linear parameter say $F$, for Doppler-broadening measurements, the mean value of this is

$$F_M = \frac{\lambda_t\kappa F_t + \lambda_b(\lambda_t + \delta)F_b}{\lambda_b\lambda_t + \lambda_t\kappa + \lambda_b\delta}, \tag{2}$$

where $F_t$ and $F_b$ are the values of the Doppler parameter for the trapped state and the bulk state, respectively. From (1) and (2) it can be seen that detrapping becomes important, if $\delta \sim \kappa \gtrsim \lambda_b$, i.e. trapping and detrapping rates are of the same order of magnitude and larger than the positron annihilation rate.

## 2. Statistical Theory of the Detrapping Rate

Conventionally the trapping rate of a positron is estimated using the Golden Rule [20]

$$\kappa = \frac{2\pi}{\hbar}\sum_{if} P(i) M_{if}^2 \delta(E_i - E_f), \tag{3}$$

where $P(i)$ is the probability of the positron to be in the initial state $i$, $M_{if}$ is the specific matrix element of the transition, and the sum goes over all initial and final states, with energies $E_i$ and $E_f$. Exchanging the meaning of the initial and final states, the same formula applies also for detrapping. The matrix elements $M_{ij}$ are the same and the difference in the trapping and detrapping rates comes from the statistical distribution of the initial states and from the density of the final states. The Golden Rule has been used in estimating the trapping rates of positron to vacancies [20], voids [21, 11] and dislocations [22, 5]. If the positron binding energy is high ($E_b \gtrsim 1\,\mathrm{eV}$) the leading transition mechanism in metals is electron-hole pair production, whereas at small binding energies acoustic phonon emission dominates. The calculated trapping rates are of the same order of magnitude as the experimental estimates.

The Golden Rule can be used equally well for calculating the absolute value of the detrapping rate. However, in interpreting the experimental results it is more important to know the ratio of the trapping and detrapping rates. The statistical physics conventionally used in chemical rate theory offers a simple and more general approach. Noticing first that $\kappa$ and the detrapping rate $\delta$ are totally independent of the annihilation rates one can tentatively substitute $\lambda_b = \lambda_t = 0$ in Fig. 1. Then in the equilibrium $\kappa n_b = \delta n_t$ ($s=0$), giving

$$\frac{\delta}{\kappa} = \frac{n_b}{n_t}. \tag{4}$$

This ratio can be calculated by requiring that the chemical potentials are the same for the trapped and the free state, or alternatively, by calculating directly the statistical occupation probabilities. We follow the latter procedure and write

$$\frac{\delta}{\kappa} = \sum_{i \in n_b} \mathrm{e}^{-\beta E_i} \Big/ \sum_{i \in n_t} \mathrm{e}^{-\beta E_j}, \tag{5}$$

where $\beta = 1/k_B T$ and $E_i$'s are the energy states of the system. The sums in the numerator and in the denominator go over energy states where the positron is free and trapped, respectively. Equation (5) is valid for all transition mechanisms and requires only the knowledge of the energy spectrum of the system. We first assume that the positron energy states are decoupled from those of the host system (electrons and phonons). Then the medium acts as a heat bath for the positron; the energy states of the medium can be factorized out in the sums of (4), i.e. $E_i$'s can be interpreted as positron energies. We return to the more general case at the end of this chapter and in the Appendix.

A good approximation for the bulk states of the positron are plane waves with an effective mass $m^*$ [23] and density of states $g(\varepsilon) = V(2m^*)^{3/2}\varepsilon^{1/2}/2\pi^2\hbar^3$, where $V$ is the volume of the system. If the positron has only one bound state in the trap with a binding energy $E_b$ the ratio of the trapping and detrapping rates is

$$\frac{\delta}{\kappa} = \frac{1}{\varrho_v}\left(\frac{m^* k_B T}{2\pi\hbar^2}\right)^{3/2} \mathrm{e}^{-E_b/k_B T}, \tag{6}$$

where $\varrho_v$ is the defect density. Equation (6) is valid for small three-dimensional traps. In more extended defects the positron may have a whole spectrum of bound states. We take up here three special cases: (i) line defects (perfect dislocations), (ii) surfaces (or grain boundaries), and (iii) volume defects (large vacancy clusters, voids). Defining the lowest bound state energy to be $-E_b$ and assuming a continuous spectrum of states up to zero binding energy with a state density of free particles of one-(i), two-(ii) or three-(iii) dimensional system, the sums in (5) can be immediately done and one obtains

$$\text{(i)}\quad \frac{\delta}{\kappa} = \frac{m^* k_B T}{\varrho_A 2\hbar^2} \frac{\mathrm{e}^{-E_b/k_B T}}{\operatorname{erf}(\sqrt{E_b/k_B T})}, \tag{7}$$

$$\text{(ii)}\quad \frac{\delta}{\kappa} = \frac{1}{\varrho_L}\left(\frac{m^* k_B T}{2\pi\hbar^2}\right)^{1/2} \frac{\mathrm{e}^{-E_b/k_B T}}{(1-\mathrm{e}^{-E_b/k_B T})}, \tag{8}$$

$$\text{(iii)}\quad \frac{\delta}{\kappa} = \frac{1}{V_T \varrho_v} \mathrm{e}^{-E_b/k_B T} \cdot \left[\frac{\sqrt{\pi}}{2} \operatorname{erf}(\sqrt{E_b/k_B T}) - \left(\frac{E_b}{k_B T}\right)^{1/2} \mathrm{e}^{-E_b/k_B T}\right]. \tag{9}$$

Above, $\varrho_A$ is the number of line defects per unit area, and $\varrho_L$ the surface to volume ratio for planar traps. In (9) $V_T$ is the volume of the trap, and it is assumed that $V_T \ll V$ but that $V_T$ is large enough to allow a quasi-continuous spectrum of bound positron states. Note that for such large defects one may have to consider the possibility of trapping during thermalization, and the interplay between diffusion and trapping is important.

Above we have assumed that the positron excitations are completely decoupled from the excitations of the system. This is not quite true especially in the case of phonon excitations [24]. In the adiabatic (Born-Oppenheimer) approximation the positron energy depends on the instantaneous ion positions. In general, we can write $E_i = E_i^l + \varepsilon_j(i)$, where $E_i^l$ is the energy of the lattice without the positron and $\varepsilon_j(i)$ is the positron energy. Then the sums in (5) can be rewritten as, e.g. for the denominator,

$$z_t = \sum_i \sum_{j \in n_t} \mathrm{e}^{-\beta E_i^l} \mathrm{e}^{-\varepsilon_j(i)} = \sum_{j \in n_t} \langle \mathrm{e}^{-\beta\varepsilon_j} \rangle, \tag{10}$$

where the brackets denote a thermal average. In the Gaussian approximation for the positron energy distribution one has

$$\langle \mathrm{e}^{-\beta\varepsilon_j} \rangle = \mathrm{e}^{-\beta\langle\varepsilon_j\rangle} \mathrm{e}^{1/2\beta^2[\langle\varepsilon_j^2\rangle - \langle\varepsilon_j\rangle^2]}. \tag{11}$$

The first exponential in (11) describes just the replacement of $\varepsilon_j$ by its thermal average, and the second arises from the fluctuations. It is easy to see that in the canonical ensemble the leading thermal energy variance is proportional to the temperature and thus both the exponentials have the same temperature dependence. The effect of the temperature dependence on the actual detrapping rate can be evaluated by simply replacing the exponential in, e.g., (6) by the expression (11).

## 3. Results and Discussion

### 3.1. *Vacancies*

In thermal equilibrium the vacancy concentration is $c_v = \exp(s_v/k_B)\exp(-\beta E_v)$, where $s_v$ and $E_v$ are the vacancy formation entropy and energy, respectively. Neglecting first the temperature dependence of the positron binding energy the positron detrapping rate can be estimated from (6).

$$\frac{\delta}{\kappa} = \Omega_0 e^{-S_v/k_B}\left(\frac{m^* k_B T}{2\pi\hbar^2}\right)^{3/2} e^{\beta(E_v - E_b)}, \tag{12}$$

where $\Omega_0$ is the volume of the unit cell of the solid. Since the entropy factor $\exp(-S_v/k_B)$ and the effective mass $m^*$ are rather independent of the metal [23], the importance of detrapping is mainly determined by the difference $E_v - E_b$[*].

From the experimental point of view the detrapping is important if $\delta/\kappa \sim 1$ in the temperature region where the trapping rate $\kappa$ becomes so high ($\sim \lambda_b$) that trapping can be detected. This characteristic temperature $T_c$ for the onset of trapping can be defined as the point where the mean lifetime (or $F$-parameter) starts to increase drastically from the more or less linear temperature dependence. McKenzie and Lichtenberger [25] have shown that there is an empirical relation between this temperature and the vacancy formation energy: $E_v \sim 14 k_B T_c$. Using this relation and taking $m^* \sim m_e$, $\Omega_0 \sim 15\,\text{Å}^3$, and $\exp(S_v/k_B) \cong 5$ representing typical metals, the two energies, $E_v$ and $E_b$, alone determine whether the detrapping can be observed. In Fig. 2 the positron binding energies which give $\delta/\kappa = 1$ and $\delta/\kappa = 10$ at $T_c$ are plotted as a function of the vacancy formation energy. Some of the theoretical estimates of the binding energies [26] are also shown in the figures. For most metals the estimated binding energies are so large [23, 26] that detrapping is unimportant. However, alkali metals, Mg, and noble metals seem to be candidates for observable detrapping, and it should thus be considered in interpreting experimental results. The reason that no trapping has been observed in alkali metals may indeed be a manifestation of a fast detrapping rate as also suggested by Tam and Siegel.

A simplified example of the effect of detrapping is shown in Fig. 3, where the mean lifetime, (1), of a "prototype" metal is plotted as a function of temperature. $\lambda_b$, $\lambda_t$, and $\nu = \kappa/c_v$ (the specific trapping rate) are assumed to be temperature independent. The solid line corresponds to a case where no detrapping occurs ($E_v = 1$ eV, $E_b = 2$ eV). If $E_b$ is decreased, the $S$-curve

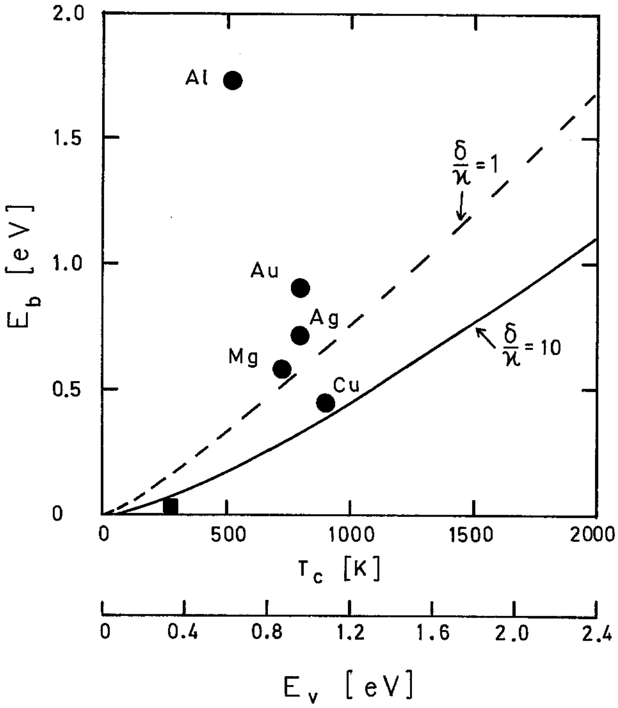

Fig. 2. Positron detrapping from vacancies in thermal equilibrium. $E_b$ is the positron binding energy and $E_v$ the vacancy formation energy. $T_c$ is defined in the text. The broken curve and the full curve give contours below which the ratio $\delta/\kappa$ is larger than 1 and 10, respectively, in the temperature region where the trapping rate becomes comparable to the annihilation rate. The black dots are estimates for different metals using experimental vacancy formation energies and calculated positron binding energies [23, 26]. The square contains all alkali metals from Li to Cs

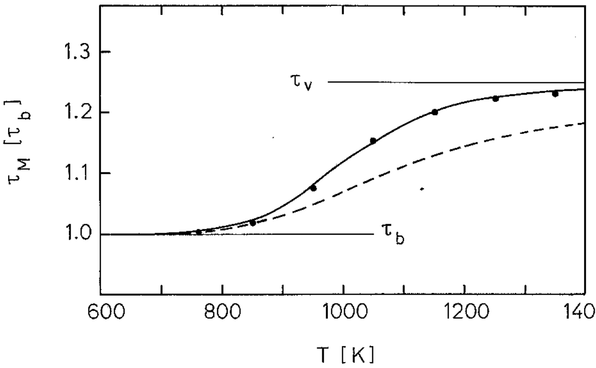

Fig. 3. The mean lifetime in prototype metals as a function of temperature. $\tau_v$ and $\tau_b$ are the vacancy and bulk lifetimes, respectively. The trapping rate is $\kappa = \kappa_0 \exp(-E_v/k_B T)$ and the detrapping rate is calculated from (12) using $\Omega_0 = 15\,\text{Å}^3$. Full curve: $\kappa_0 = 10^5\,\text{s}^{-1}$, $E_v = 1$ eV, $E_b = 2$ eV. Broken curve: $\kappa_0 = 10^5\,\text{s}^{-1}$, $E_v = 1$ eV, $E_b = 0.4$ eV. Black dots: $\kappa_0 \doteq 10^6\,\text{s}^{-1}$, $E_v = 1.19$ eV, $E_b = 0.82$ eV

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[*] If $E_v > E_b$ the ratio diverges at low temperature but since $\kappa \propto C_v$ the detrapping rate $\delta$ goes to zero at $T = 0$

flattens, as shown by the dashed line ($E_b = 0.5$ eV). The black dots show a case where $E_v = 1.19$ eV, $E_b = 0.82$ eV, and demonstrate that the existence of possible detrapping is very difficult to see from the $S$-curve. The experimental accuracy is usually not enough to allow one to determine the temperature dependence of the prefactor of the exponential [27], and in a realistic case this is even more complicated due to the temperature dependence of $\lambda_b$ and $\lambda_t$. In general, neglecting detrapping (if important) leads to a too small value for the vacancy formation energy. If the positron binding energy depends on temperature, (10) has to be used in calculating $\delta/\kappa$. The binding energy will be affected by thermal expansion and by lattice vibrations which in the adiabatic approximation change the positron energy levels both in the bulk and in the trap. In the Appendix we have derived approximate formulae for the change in the positron-vacancy binding energy due to harmonic lattice vibrations, and for the variance of the binding energy. The results indicate that the lattice vibrations change the binding energy typically as much as the thermal expansion estimated by Gupta and Siegel [28] but in the opposite direction. The relative importance of lattice vibrations in calculating annihilation parameters was first pointed out by Stott and Kubica [24]. Also it is shown in the Appendix that the fluctuations in the binding energy may also have a dominant role in determining the detrapping rate.

The vacancy formation energies measured by other methods seem in general to be in good agreement with the values from positron annihilation experiments [29, 19], indicating that detrapping is unimportant in most metals. However, since the theoretical *estimates* of positron binding energies in many metals (alkalis, Mg, Cu, Ag, Au) are rather small, the existence of detrapping from vacancies in some metals is not totally ruled out. Hautojärvi et al. [30] have made an experimental detrapping analysis for Mg. They were able to confirm the theoretical estimate of the small positron binding energy, but could not extract the possible effect of detrapping on the results.

### *3.2. Dislocations and Grain Boundaries*

For line defects (dislocations) and for planar defects (e.g. grain boundaries, stacking faults) the detrapping rates can be calculated from (7) and (8), respectively. Also in these cases the temperature dependence of the detrapping is governed by the exponential $\exp(-\beta E_b)$, where $E_b$ is now the binding energy of the deepest bound state. In Fig. 4 and 5 we show the $E_b$ versus $T$ curves which give $\delta/\kappa = 1$ for different densities of line and planar defects. In the region below each curve detrapping is dominating.

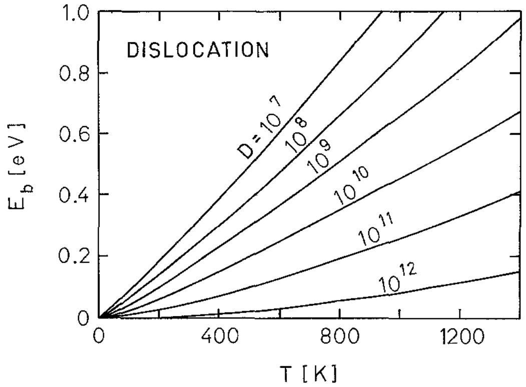

Fig. 4. Contours at which the trapping rate equals the detrapping rate. Below each curve the detrapping rate dominates. $E_b$ is the positron binding energy, $T$ the temperature, and $D = \varrho_A$ the dislocation density [cm$^{-2}$]

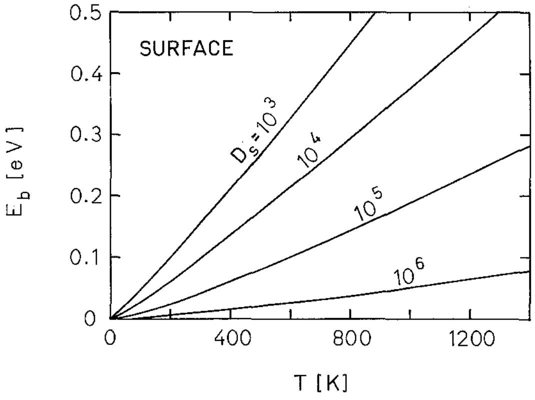

Fig. 5. Contours at which the trapping rate equals the detrapping rate. Below each curve the detrapping dominates. $E_b$ is the positron binding energy, $T$ the temperature, and $D_s = \varrho_L$ [cm$^{-1}$] area to volume ratio of internal surfaces (grain boundaries or stacking faults)

In reality dislocations and grain boundaries are not ideal but typically contain vacancy-type defects (jogs, kinks etc.) which may localize the positron. In this case a dislocation or a grain boundary may form a percursor state to the final trap. This possibility has been studied more closely by Smedskjaer et al. [5]. Another interesting possibility is that line or planar defects act as shallow traps which at low temperature present the positron capture into other traps in the sample via "shielding" [4, 31]. The key idea in both cases is the assumption that the positron trapping rate, which usually increases with the binding energy [20–22], can in these traps with a large spatial extent become large enough already at very small binding energies and defect densities. The model calculations of Smedskjaer et al. [5] indicated that this is indeed possible for the case of dislocations.

### 3.3. *Positronium Desorption from a Surface*

Positrons may get trapped in an image-potential-induced surface state [32, 33] near a solid-vacuum interface. In principle, detrapping is possible either into the vacuum or the bulk. Inside metals, positronium (Ps) formation is not allowed; if $E_s$ is the binding energy of the surface state with respect to vacuum, the activation energy for the escape as $e^+$ into the bulk is $E_s - \phi_+$, where $\phi_+$ is the positron work function. If $\phi_+ > E_s$, the surface state actually becomes unstable. Detrapping from the surface to the bulk is not directly observable, but could be seen as increased annihilations in bulk relative to those in the surface state.

On the other hand, detrapping from the surface to the vacuum is readily observed as enhanced positronium formation on the surface [2, 3]. Since the electron work functions $\phi_-$ universally are less than the positronium binding energy of 6.8 eV, the energetically favored desorption route is as positronium. The activation energy for the process is

$$E_A = E_S + \phi_- - 6.8\,\text{eV}. \tag{13}$$

For a number of cases, this seems to be clearly the dominant mechanism. Experimental values for the activation energy are in reasonable agreement with theoretical estimates [33]. In the experiments a low-energy positron beam strikes the surface. After implantation and thermalization a sizable portion of the positrons diffuse back to the entrance surface, and may spontaneously leave the solid either as $e^+$ or Ps, or may trap at the surface. The fraction emitted as Ps is gauged and is seen to rise with temperature following an activation curve. The velocity distribution of the emitted Ps can also be clearly decomposed into a non-thermal (fast) and a thermal component [34]. Consequently the thermal desorption of Ps constitutes the only case of positron detrapping unambiguously observed experimentally. Theoretical aspects of positron surface processes have been discussed at length recently [35, 36].

In order to use the approach outlined above in the analysis of Ps desorption one has to assume that the positron stays trapped long enough to achieve thermal equilibrium. A related problem in the case of desorption of molecules has been discussed by e.g. Iche and Nozieres [37].

One can obtain the escape rate [38] from detailed balance arguments by using (4), where $\kappa$ should now be interpreted as the capture rate of a free Ps in vacuum into a positron surface state and an electron in the bulk solid. Alternatively, one can calculate the density of positronium atoms $n_{\text{Ps}}$ outside the surface in equilibrium and obtain the emitted (or absorbed) flux as

$$n_{\text{Ps}} \langle V_Z[1 - R(V_Z)] \rangle_{V_Z > 0}, \tag{14}$$

where $R(V_Z)$ is the reflection coefficient of the surface for Ps atoms having velocity $V_Z$ normal to the surface. The pointed brackets in (14) denote a thermal average. Either way we obtain the desorption rate (neglecting for the moment the temperature dependence of the activation energy) for a Boltzmann distribution of Ps velocities and surface positrons free to move parallel to the surface,

$$\delta = \frac{4}{h^2}(2\pi M k_B T)^{1/2} e^{-E_a/k_B T} \langle V_Z[1 - R(V_Z)] \rangle, \tag{15}$$

where $M = 2m$ is the Ps mass.

For a "blackbody" surface $R(V_Z) \equiv 0$, and we obtain the maximum desorption rate

$$\delta_{bb} = \frac{4}{h} k_B T e^{-E_a/k_B T} = 8.33 \cdot 10^{10} \cdot T[\text{K}] e^{-E_a/k_B T} s^{-1}. \tag{16}$$

Let us write generally

$$1 - R(V_Z) = S_0 + \left(\frac{V_Z}{V_0}\right)^n, \tag{17}$$

where $S_0$ is the sticking coefficient at zero velocity. Using (15) we find

$$\delta = S_0 \cdot \delta_{bb} + \frac{4 \cdot \Gamma\left(\frac{n+4}{2}\right)}{(n+2) h V_0^n M^{n/2}} (2k_B T)^{\frac{n}{2}+1} e^{-E_a/k_B T}, \tag{18}$$

where $\Gamma(x)$ is the gamma function.

The time-of-flight experiments of Mills and Pfeiffer [34] for Cu(111) indicate that $n = 2$, which is in accord with the semiclassical arguments [11] about trapping and reflection. The absolute value of the sticking coefficient has not been established, but Mills and Pfeiffer find that $\sqrt{S_0} \cdot V_0 = 8.7 \cdot 10^6$ cm/s, and the data suggests that $S_0$ is probably less than 0.1.

If the positrons trapped at the surface are localized also in the surface plane (i.e. in surface defects), the desorption rate is

$$\delta^{\text{def}} = S_0 \cdot \delta_{bb}^{\text{def}} + \frac{2^{n+1}}{(n+2)} \frac{\Gamma\left(\frac{n+4}{2}\right)}{\varrho_v^s h^3} \frac{(k_B T)^{\frac{n}{2}+2}}{M^{\frac{n}{2}-1}} e^{-E_a/k_B T}, \tag{19}$$

where $\varrho_v^s$ is the surface density of traps, and the "blackbody" rate is

$$\delta_{bb}^{\text{def}} = \frac{\pi}{h^2} (k_B T)^2 \frac{M}{\varrho_v^s} e^{-E_a/k_B T}. \tag{20}$$

We note that an experimental determination of the temperature dependence of the desorption rate can in principle, via (15)–(20), establish the nature of the surface state (whether free in two dimensions or not). Unfortunately the data obtained so far is not accurate enough for a determination of exponent of temperature in the prefactor, but the observed excape probability $\delta/(\delta+\lambda_s)$, where $\lambda_s$ is the annihilation rate in the surface state, is in good qualitative agreement with the expressions (18) or (19) when $n=2$. Note that the analysis is made even more difficult by the temperature dependences (though relatively weak) of the implantation profile and the positron diffusion coefficient [35]. The prompt (nonthermal) Ps and $e^+$ yields also have a temperature dependence through the reflection coefficient of the surface for positrons reaching it from the bulk [35].

If the activation energy $E_a$ has a temperature dependent distribution through those of the binding energy $E_S$ and the electron work function $\phi_-$, the desorption rate is further modified in a way completely analogous to vacancy case discussed in the Appendix. The temperature dependence and fluctuations of $E_a$ may actually raise the desorption rate to be larger than the thermodynamic "blackbody" limit indicated in (16) and (20).

## 4. Summary and Conclusions

Starting from the statistical probability distribution of positrons in a metal containing defects we have derived formulas for positron detrapping from vacancies, dislocations and surfaces. In thermal equilibrium measurements the importance of the detrapping from vacancies has been related to the difference between the vacancy formation energy and the positron binding energy. Fluctuations in the positron binding energy at elevated temperatures were found to have a notable effect on the detrapping rate. Theoretical estimates for the positron binding energy indicate that in equilibrium vacancy concentration the detrapping rate exceeds clearly the trapping rate in alkali metals.

For typical dislocation and grain boundary densities detrapping from these defects is important only if the positron binding energy is about 0.1 eV or less. Most clearly detrapping from these shallow traps can be observed indirectly as an enhancement in the apparent positron mobility or, in the case of a precursor state, as a decrease in the trapping rate into the final trap.

Formulae for positronium desorption from a metal surface were derived assuming quite a general velocity dependent sticking coefficient for Ps and considering both delocalized and localized surfaces states. A semiclassical sticking coefficient yields good agreement with existing experimental results, but no distinction can be made whether the positron is free or localized at the surface.

## Appendix

### *Temperature Dependence of the Positron Energy in a Vacancy*

We want to estimate the effect of the vibrations of the neighbouring atoms on the mean positron energy and its variance when the positron is trapped in a vacancy. For simplicity we approximate the positron lattice (pseudo)-potential by a contact interaction $V_0\delta(\bar{r}-\bar{R}_i)$ where $\bar{R}_i$ denotes a lattice site. Using first order perturbation theory and assuming that the atoms move independently the mean energy change due to *lattice vibrations* is

$$\langle E_b\rangle - E_b = \sum_i \left[\int d\bar{r} P_i(\bar{r}) V_0 |\psi_+(\bar{r})|^2 - V_0|\psi(\bar{R}_i^0)|^2\right], \qquad \text{(A.1)}$$

where $P_i(\bar{r})$ is the probability that the ion $i$ is in the position $\bar{r}$, $\psi_+$ is the positron wave function, and $\bar{R}_i^0$ the equilibrium lattice site. We use the harmonic approximation for the lattice vibrations, $P_i(\bar{r}) \propto \exp(-|\bar{r}-\bar{R}_i^0|^2/2\sigma^2)$, and the positron wave function outside the vacancy is taken to be $\psi_+(r)=A\exp(-\sqrt{2E_b}r)$ where $E_b$ is the zero-temperature binding energy, and $A$ constant. With a these approximations we obtain

$$(\langle E_b\rangle - E_b)_{\text{vibr}} = \sum_i 4V_0 E_b \sigma^2 |\psi_+(R_i^0)|^2 . \qquad \text{(A.2)}$$

Similarly one can calculate the variance

$$\langle E_b^2\rangle - \langle E_b\rangle^2 = \sum_i 4V_0^2 E_b \sigma^2 |\psi_+(R_i^0)|^4 . \qquad \text{(A.3)}$$

To give an estimate for $V_0$ we can calculate in the same manner the energy change due to *thermal lattice expansion*:

$$(\langle E_b\rangle - E_b)_{\text{expansion}} = -\sum_i 2V_0\sqrt{2E_b}\cdot \alpha T R_i^0 |\psi_+(R_i^0)|^2 . \qquad \text{(A.4)}$$

where $\alpha$ is the linear expansion coefficient. We note that the effect of vibrations and thermal expansion on the mean binding energy and thus to the detrapping rate are opposite: the former tends to decrease detrapping, while the latter enhances it.

Gupta and Siegel [28] have calculated from first principles the effect of lattice expansion on the positron binding energy in Al vacancy. From their values,

$E_b = 3.36\,\text{eV}$

and

$\partial E_b/\partial T = -4.2\times 10^{-4}\,\text{eV K}^{-1}$,

we first obtain $(\langle E_b\rangle - E_b)/k_B T = -6.7$ for lattice expansion. Using (A.4) we can obtain the product $V_0 A^2$ and then from (A.2) and (A.3), calculate estimates from the mean energy change and the binding energy variance due to harmonic lattice vibrations. Assuming the amplitude of the vibrations to be $\sigma(T)=(9T/Mk_B\theta_D^2)^{1/2}$, where $M$ is the atom mass and $\theta_D$ the Debye temperature, one obtains at $T=700\,\text{K}$:

$(\langle E_b\rangle - E_b)_{vib}/k_b T = 6$

and

$(\langle E_b^2\rangle - \langle E_b\rangle^2)/2(k_B T)^2 = 12$.

These estimates would indicate that the detrapping rate is smaller by a factor of $\exp(-12)$ smaller than in a static lattice. The dominant effect of fluctuations is underscored in this example. However, if the positron binding energy were smaller, e.g. $E_b=0.3\,\text{eV}$, keeping all other constants the same yields

$(\langle E_b\rangle - E_b)_{vib}/k_B T = 0.7$

and

$(\langle E_b^2\rangle - \langle E_b\rangle^2)/2(k_B T)^2 = 1.4$, leading (with lattice expansion) to an *increased* detrapping rate. One can conclude that accurate values of the prefactor in the detrapping rate expression are difficult to obtain, as they require detailed information of the temperature dependence of the positron-defect coupling. The effect of lattice vibrations is to decrease thermal escape from the defect, whereas anharmonic lattice expansion generally increases detrapping. The fluctuations in the positron binding energy always lead to a decrease in the detrapping rate.

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