PHYSICAL REVIEW B VOLUME 49, NUMBER 3 15 JANUARY 1994-I

Comment on "Multiple encounters of thermal positrons with surfaces"

Kjeld O. Jensen
Department of Physics, University of Essex, Colchester CO4 3SQ, United Kingdom

Alison B. Walker
School of Physics, University of East Anglia, Norwich NR4 7TJ, United Kingdom

(Received 1 June 1992; revised manuscript received 23 March 1993)

We point out that the standard diffusion model for the motion of thermalized positron does take into account multiple encounters of the positron with the surface, contrary to what could be inferred from a recent paper by Kong and Lynn [Phys. Rev. B **44**, 13 109 (1991)]. In this context we discuss recent measurements on positron-surface interactions and positron Auger spectroscopy.

In positron beam experiments, positrons are implanted with eV or keV energies into the target. After rapid thermalization, some of the positrons diffuse back to the surface before either entering one of the three surface channels (i) emission as free positron, (ii) emission as positronium (Ps) atoms, (iii) trapping into the image potential induced surface state, or (iv) being reflected from the surface, see Fig. 1. If reflection occurs, the positrons will on average scatter off a phonon at a distance of the order of the mean free path from the surface. Since the dominant scattering process, i.e., acoustic-phonon scattering, is isotropic, many of the reflected positrons will return to the surface. Hence, any treatment of positron surface interactions should allow for the possibility of multiple encounters with the surface as was pointed out by Kong and Lynn.[1]

In this Comment, we emphasize that the standard "diffusion model," specified by Eqs. (1) and (2) below, in which the diffusion equation is used to calculate the probability for the positron returning to the surface, *does* allow for the multiple surface encounters, contrary to what could be inferred from the discussion by Kong and Lynn[1] of the experimental results in Refs. 2–5. The importance of this result lies in the extensive use of the diffusion model in interpretation of experimental results for positron beams, examples being: positron emission from thin films;[2,3] Ps formation and positron emission at surfaces;[4–6] near surface defect profiling;[7] and positron trapping into voids.[8] Kong and Lynn discussed some of these aspects,[1] with especial reference to the first two examples listed above, and also suggested that the signal observed in positron annihilation induced Auger electron spectroscopy (PAES) may partly come from positrons annihilating near the surface, rather than from those trapped into the surface state. Below, we reexamine their conclusions in the light of our interpretation of the diffusion model.

The diffusion model is based on solutions to the positron diffusion equation in a semi-infinite uniform medium or in thin films, namely,

$$\frac{\partial n(z,t)}{\partial t} - \lambda n(z,t) = D\frac{\partial^2 n(z,t)}{\partial z^2}, \qquad (1)$$

where n is the positron density, z the distance from the surface, t the time, λ the bulk annihilation rate, and D the positron diffusion constant. The boundary condition at the surface (z=0) is

$$D\left.\frac{\partial n}{\partial z}\right|_{z=0} = \nu n(0,t), \qquad (2)$$

where ν is the probability per second for the positron to make the transition from the diffusing bulk positron state inside the surface to one of the three surface channels. For thin films, a similar boundary condition applies at the other surface of the film.

Since ν is the transition rate per unit surface area per unit positron density it has the dimension of a velocity. It can be related directly to the total probability for surface trapping or emission *per surface encounter* P_{enc} as[9,10]

$$P_{\text{enc}} = 1 - \exp(-\nu/v_z), \qquad (3)$$

where v_z is the positron velocity perpendicular to the

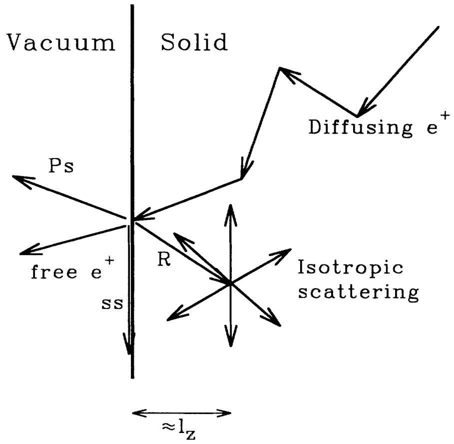

FIG. 1. Schematic picture of positron-surface interactions. The labels Ps, free e^+, and ss refer to the three surface channels described in the text. The label R indicates a reflected positron and l_z is the mean distance traveled normal to the surface before scattering.

0163-1829/94/49(3)/2215(3)/$06.00

surface. It is important to note that the diffusion equation with the boundary condition in Eq. (2) describes the random walk of the positron in the solid both before its first encounter with the surface and after one or several reflections.

From solving the diffusion equation, one obtains the standard result[7] for the probability $P_{\rm escape}$ for a positron with implantation profile $n_0(z)$ escaping the bulk and entering one of the three surface channels:

$$P_{\rm escape} = \frac{1}{1+D/(\nu L)} \int_0^\infty dz\, n_0(z) \exp(-z/L), \qquad (4)$$

where $L = \sqrt{D/\lambda}$ is the diffusion length. Thus the diffusion model provides a well-defined prescription for determining $P_{\rm enc}$, and thus the reflection coefficient R ($= 1 - P_{\rm enc}$): from measurements of $P_{\rm escape}$ Eq. (4) can be used to deduce ν, which can then be translated into a probability per surface encounter by using Eq. (3).

In Kong and Lynn[1] it was suggested that the diffusion model assumes that the reflected positrons do not contribute to positron surface processes. The discussion above shows that this is not correct. To further emphasize this point we will in the following show that an alternative analysis along the lines of that presented in Ref. 1 can be used to give an approximate derivation of Eq. (4).

The probability obtained from the diffusion equation that a positron will reach the surface at least once is $\int_0^\infty dz\, n_0(z) \exp(-z/L)$. If the positron is reflected, it will initially be moving away from the surface. At an average depth of $l_z = \tau_{\rm sc} v_z$, where $\tau_{\rm sc}$ is the scattering time, it will suffer a scattering event (Fig. 1). The dominant scattering mechanism in metals and semiconductors is normally acoustic-phonon scattering[11,12] which is nearly isotropic. Hence, the velocity distribution after the first scattering will be approximately isotropic. If one assumes that the motion after this first scattering event can be described by the diffusion equation from an initial distribution $\exp(-z/l_z)/l_z$, the probability of the positron returning to the surface is

$$P_{\rm return} = \int_0^\infty \frac{\exp(-z/l_z)}{l_z} \exp(-z/L) = \frac{L}{L+l_z} \quad . \qquad (5)$$

This is the quantity denoted α in Ref. 1. For defect-free metals or semiconductors near room temperature L is of the order of 1000 Å while l_z will be of order 10 Å. Thus, $P_{\rm return}$ will be ≈0.99 as conjectured in Ref. 1.

The escape probability is, cf. Eq. (3) of Ref. 1,

$$\begin{aligned} P_{\rm escape} &= \int_0^\infty dz\, n_0(z) \exp(-z/L)\, P_{\rm enc} \sum_{i=0}^{\infty} \left[(1-P_{\rm enc}) \frac{L}{L+l_z} \right]^i \\ &= \int_0^\infty dz\, n_0(z) \exp(-z/L) \Big/ \left[1 + \frac{l_z}{l_z+L} \frac{1-P_{\rm enc}}{P_{\rm enc}} \right] \quad . \end{aligned} \qquad (6)$$

For small $P_{\rm enc}$ and hence strong reflection $(1-P_{\rm enc})/P_{\rm enc} \approx v_z/\nu$, cf. Eq. (3). The length l_z will be comparable to the mean-free path and hence much smaller than L. We can thus approximate $l_z/(l_z+L)$ by l_z/L. If we write the diffusion constant as[12] $D = (v^2/3)\tau_{\rm sc}$ where v is the average positron velocity which for an isotropic velocity distribution becomes $D = v_z^2 \tau_{\rm sc}$, we get

$$\frac{l_z}{l_z+L} \frac{1-P_{\rm enc}}{P_{\rm enc}} \approx \frac{D}{\nu L} \quad . \qquad (7)$$

When this is inserted in Eq. (6) we recover the exact result for $P_{\rm escape}$, derived from the diffusion equation, given in Eq. (4).

In the light of this analysis, we would argue that Britton and co-workers[4,5] and Brandes and co-workers,[2,3] who solve the diffusion equation with boundary conditions given by Eq. (2) to determine positron emission from thin films and positron surface branching ratios, respectively, do take into account multiple reflections at the surface. In particular, the values of ν for metals (Cu, Al, Ag) of the order of 10^3–10^4 m/s, deduced in Refs. 4, 5, and 8, are those for single encounters. Hence, one may determine the reflection coefficient R ($= 1 - P_{\rm enc}$) through Eq. (3). However, it appears that Britton and coworkers[4,5] did not use Eq. (3) but assumed (incorrectly) that ν and $P_{\rm enc}$ were proportional with a proportionality constant which is independent of the positron velocity. If Eq. (3) *is* used to relate the experimentally deduced values of ν (Refs. 5 and 8) to $P_{\rm enc}$, we obtain $P_{\rm enc}$ at room temperature of the order of 0.01–0.1 in accordance with theoretical estimates.[1,10]

Brandes and co-workers[2,3] do not give enough details of their calculations to establish how they derived $P_{\rm enc}$ from their solution of the diffusion equation for thin Ni films. We therefore cannot establish whether the value of R of 0.63 deduced in Ref. 3 is consistent with the above analysis.

Kong and Lynn[1] have argued that surface reflection plays a significant role in PAES measurements. In PAES experiments, the majority of the signal arises from positrons trapped at the surface annihilating with core electrons, creating core holes which relax by the Auger process.[13] However, there could be a contribution from bulk positrons annihilating within an Auger electron escape depth of the surface. This contribution was invoked in Ref. 1 to explain the result of Soininen, Schwab, and Lynn[14] that there is significant intensity of the PAES signal for Ge(100) at high temperatures where most of the surface trapped positrons would be desorbed as Ps. In the following we argue that this explanation is unlikely.

Considering first only thermalized positrons, the fraction of positrons annihilating in the bulk of a sample in positron experiments can be estimated from Eq. (4). For the implantation energies below 50 eV normally employed in PAES, the implantation depth will be much smaller than L. Hence, the integral in Eq. (4) will be close to unity. Since the PAES intensities for Ge are comparable to those of Cu,[14] indicating that the fraction of positrons annihilating from the surface state is similar, the value of ν for Ge must be of the same order of magnitude as those deduced for metals, i.e., 10^3–10^4 m/s. For $\lambda = 10^{10}$ s^{-1} and $D = 10^{-4}$ m^2/s (typical values) this range of ν leads to P_{escape} values of 0.5–0.9 indicating that 10–50 % annihilate in the bulk.

This bulk contribution will clearly be important in experiments which are sensitive to positrons annihilating anywhere in or near the sample such as Doppler broadening or positron lifetime measurements. However, only a fraction of these will annihilate close enough to the surface for the Auger electrons in PAES experiments to escape. Using a semiclassical model for positrons, a positron moving at thermal velocity ($\approx 10^5$ m/s) will spend about 10^{-14} s within an Auger electron escape depth, $\approx$ 10 Å, of the surface at each surface encounter. Assuming $\lambda = 10^{10}$ s^{-1}, this corresponds to an annihilation probability per encounter of $\approx 10^{-4}$, which is 2–3 orders of magnitude lower than the estimated P_{enc} of 0.01–0.1, which includes the possibility of trapping into the surface state. This suggests that the ratio of the number of positrons annihilating in the top 10 Å to the number undergoing other surface processes (surface trapping, Ps formation) is only 0.001–0.01. In addition, the quantum reflection at the surface step would tend to reduce the probability of bulk annihilation with electrons near the surface compared with this classical estimate since, if the reflection coefficient $1-P_{\text{enc}}$ is high, the amplitude of the positron wave function at the reflecting potential step is correspondingly low.

At the low implantation energies used in PAES, a very large fraction of positrons returns to the surface before they have thermalized.[15,16] Escape and trapping probabilities at nonthermal energies are predicted[10] to be substantially higher than at thermal energy. This means that a large fraction of positrons could be trapped on their first return to the surface when their greater energy makes surface reflection less important. Therefore, the contribution of the PAES signal from positrons annihilating close to rather than at the surface is further reduced by the possibility of epithermal trapping into the surface state. It would require further work to establish the importance of this effect, e.g., Monte Carlo simulations of low-energy positron implantation[16] coupled with a model of the energy dependence of the positron-surface interaction.[10] However, the arguments given here make it seem unlikely that the bulk contribution to the PAES signals could be as high as 5% of the total signal as is suggested in Ref. 1 to explain the temperature dependence of the PAES signal for Ge measured by Soininen, Schwab, and Lynn.[14]

In conclusion, we have shown that the diffusion model used to analyze experimental data in positron beam experiments does take into account multiple encounters of positrons with the surface and it provides a straightforward method for experimental determination of the probabilities for surface trapping or emission *per surface encounter*. The suggestion by Kong and Lynn[1] that one needs to go beyond the diffusion model to take account of multiple encounter effects therefore does not hold. We have also estimated that the contribution to PAES signal from bulk annihilations is very small and is unlikely to be able to explain the high-temperature PAES intensities for the Ge(100) surface observed by Soininen, Schwab, and Lynn.[14]

We would like to acknowledge the authors of Ref. 1 for a number of stimulating discussions.

---

[1] Y. Kong and K.G. Lynn, Phys. Rev. B **44**, 13 109 (1991).

[2] G.R. Brandes, K.F. Canter, and A.P. Mills, Phys. Rev. B **43**, 10 103 (1991).

[3] G.R. Brandes, Phys. Rev. B **43**, 10 111 (1991).

[4] D.T. Britton, P.A. Huttunen, J.A. Mäkinen, E. Soininen, and A. Vehanen, Phys. Rev. Lett. **62**, 2413 (1989).

[5] P. Huttunen, J.A. Mäkinen, D.T. Britton, E. Soininen, and A. Vehanen, Phys. Rev. B **42**, 1560 (1990).

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

[7] K.G. Lynn, in *Positron Solid State Physics*, edited by W. Brandt and A. Dupasquier (North-Holland, Amsterdam, 1983).

[8] K.O. Jensen, M. Eldrup, S. Linderoth, and J.H. Evans, J. Phys. Condens. Matter **2**, 2081 (1990).

[9] Z.W. Gortel and J. Szymański, Phys. Lett. A **147**, 59 (1990); Phys. Rev. B **43**, 1919 (1990).

[10] A.B. Walker, K.O. Jensen, D. Neilson, and J. Szymański, Phys. Rev. B **46**, 1687 (1992).

[11] E. Soininen, H. Huomo, P. Huttunen, J. Mäkinen, and P. Hautojärvi, Phys. Rev. B **41**, 6227 (1990).

[12] B. Bergersen, E. Pajanne, P. Kubica, M.J. Stott, and C. Hodges, Solid State Commun. **15**, 1377 (1974).

[13] D. Mehl, A.R. Köymen, K.O Jensen, F. Gotwald, and A. Weiss, Phys. Rev. B **41**, 799 (1990).

[14] E. Soininen, A. Schwab, and K.G. Lynn, Phys. Rev. B **43**, 10 051 (1991).

[15] B. Nielsen, K.G. Lynn, and Y.-C. Chen, Phys. Rev. Lett. **57**, 1789 (1986).

[16] K.O. Jensen and A.B. Walker, in *Proceedings of the 9th International Conference on Positron Annihilation*, edited by Zs. Kajcsos and Cs. Szeles (Trans Tech, Aedermannsdorf, Switzerland, 1992), p. 317.