Positron diffusion in Mo: The role of epithermal positrons

H. Huomo, A. Vehanen, M. D. Bentzon,* and P. Hautojärvi
Laboratory of Physics, Helsinki University of Technology, 02150 Espoo, Finland
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Positrons at keV energies, incident on Mo(111) are observed to escape the sample prior to thermalization. Analysis of positron back-diffusion data shows that an excess contribution of "hot" positronium (Ps) seriously affects positron mobility measurements. Suppressing the "hot" Ps fraction the positron diffusion coefficient is shown to vary as $T^{-0.50(4)}$. The positron implantation profile possesses a shape of a derivative of a Gaussian function. The implications of these observations to related experiments are discussed.

Recently, slow positron beams have been used to measure positron diffusion properties in bulk samples and to obtain information on positron trapping into lattice defects.[1] In most experiments the measured quantity is the positron back-diffusion probability $J(E)$, which also depends on the positron diffusion coefficient D_+, on near-surface lattice defects and on the positron implantation profile $P(z,E)$. The positron mobility is expected to be governed by acoustic phonon scattering, resulting in a $T^{-1/2}$ temperature dependence for D_+.[2] The positron implantation profile can be expressed as

$$P(z,E) = -d/dz\{\exp[-(z/z_0)^m]\} ,$$

where $z_0 = AE^n$, and A depends on the density of the sample.[3] The parameter m has been thought to be $m=1$, corresponding to an exponential implantation profile.[1]

A wide compilation of positron diffusion data in various single crystals were shown[4] to give a much stronger temperature dependence for D_+, ranging from $T^{-0.8}$ to $T^{-2.6}$. Positron-electron scattering would result in a T^{-1} law, but it is estimated to be weak as compared to phonon scattering.[2] However, if nonadiabatic behavior of the positron screening cloud is included, a much stronger than $T^{-1/2}$ dependence for D_+ will follow. For positive muon diffusion a calculation[5] yields $D_+^{\text{muon}} \propto T^{-0.7}$–$T^{-0.9}$. In the positron case, however, this effect is estimated to be unimportant.[6]

The experimental observations on positron stopping are not unambiguous. Fits to experimental back-diffusion data showed that the parameters m and n are highly correlated,[7] and they also have an apparent temperature dependence.[8] Computer simulations[3] yield $m \approx 2$, which corresponds to an implantation profile with a shape of a derivative of a Gaussian function. The parameter n has been determined by positron transmission measurements[9] and by simulations[3] to range from $n=1.4$ to 1.7, and A is in the range 3.3 to 5 μg/cm^2.[10] Our recent annihilation lineshape measurements in a multilayer ZnS/Al_2O_3 structure give direct evidence that the positron implantation profile has a Gaussian shape with $m=2.0(1)$ and $z_0 = [4.5(4)\ \mu\text{g/cm}^2]E^n$, with $n=1.62(5)$ in our experimental conditions at energies $E_{\text{inc}} = 4$ to 25 keV.[11]

In this Brief Report we show that fast escape processes of positrons and positronium (Ps) obscure positron diffusion measurements up to incident positron energies $E \approx 4$ keV in Mo(111). The reemitted positron energy distribution shows a very distinct behavior with a maximum at about 0.5 eV above the elastic threshold. After proper suppression of the Ps contribution arising from various nonlinear Ps formation mechanisms (see, e.g., Mills in Ref. 1), we show that the thermal positron diffusion resumes the $T^{-1/2}$ temperature dependence. In addition, the implantation profile of positrons can be best described by the Gaussian ($m=2$) shape with $n=1.55$. The implications of these observations to related experiments are discussed.

The experiments were done with a high-intensity slow positron beam in ultrahigh vacuum.[12] The positron back-diffusion probability was measured from the observed positronium fraction f versus the incident positron energy E.[1,13] Reemitted positrons were turned back to the sample by a retarding grid at +20 V bias respect to the sample. In each measurement about 40 000 counts were acquired to the 511-keV peak, and the measurements at 500 K contained 160 000 counts. The Mo(111) single crystal (Materials Research) was of 99.99% purity (main impurities: substitutional W 70 ppm, interstitial C 10 ppm). Prior to measurements it was annealed at 2000 °C at 10^{-8} torr.

Figure 1 shows two positron reemission energy spectra taken at incident energies 900 eV and 2 keV. These spectra were measured with a retarding field analyzer, which gives[14] only the kinetic energy $E_{\parallel}$ arising from the reemitted positron velocity parallel to the axial magnetic field. For the positron work function[1] we measure a value $\Phi = -3.0(1)$ eV. Figure 1 shows that at 900 eV about 5 to 7 % of incident positrons have more kinetic energy than the work function ($-\Phi$). The mean positron residence time can be estimated to be about 5 psec at 900 eV.[1] This time is roughly equal to the calculated thermalization time 6.8 psec at 300 K.[15] Therefore it seems evident that a fraction of positrons has not had enough time to thermalize before returning to the surface. Similar behavior in Al and Cu at small energies E has been recently observed by Nielsen *et al.*[16] and in Ni and W at $E \approx 4$ keV by Gullikson *et al.*[14] Our measurements in Cu (unpublished) show epithermal positron reemission up to incident energies $E \approx 7$ keV.

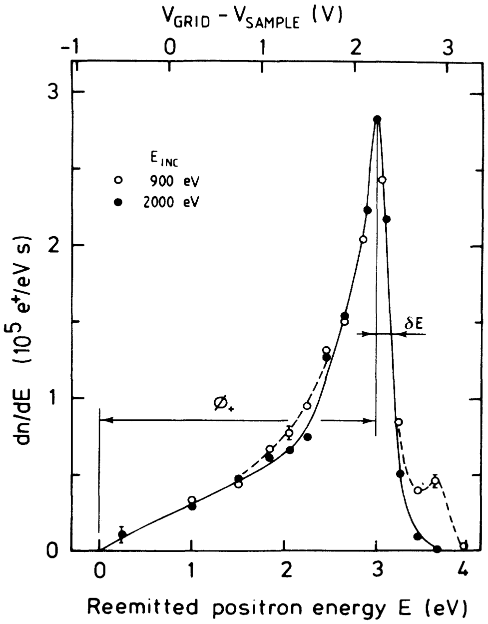

FIG. 1. The positron reemission energy spectra are shown at 900 and 2 keV incident positron energies. Small fraction of positrons is clearly seen to return back to the entrance surface before complete thermalization in case of 900 eV implantation energy.

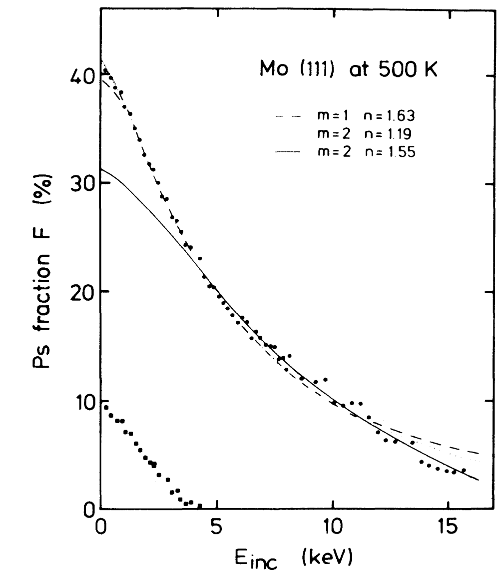

FIG. 2. Several fits (see text) to high statistics Ps fraction data $f(E)$ in Mo(111) at 500 K. The solid line is a fit, where only data above $E=4$ keV are included.

The data in Fig. 1 show that the epithermal positrons have a distinct energy distribution above the elastic threshold. Recently, the positrons emitted from rare-gas solid films are also found to exhibit a very sharp epithermal energy spectrum.[17] On the other hand, Nielsen *et al.*[16] find that epithermal $dN/dE_{\parallel}$ is a monotonously decreasing function after 50 and 300 eV positron implantation in Al(111). Careful measurements of the energy spectrum of epithermal positrons should be performed to obtain new information on the positron slowing down mechanisms. This technique is also expected to reveal new features on the electronic properties of the sample.[16,17]

Bearing the previous observations in mind, we analyzed the positron mobility data $f(E)$ taken at 300—1450 K. Within the one-dimensional diffusion model[1] the backdiffusion probability $J(E)=f(E)/f(0)$ is a Laplace transform of $P(z,E)$. The analysis routine involves multiparameter nonlinear least-squares fitting, and it enables fits to $f(E)$ data by varying only selected or all free parameters E_0, $f(0)$, m, and n.[1,13] For the parameter A we adopt a value $A=4.7\ \mu g/cm^2$.[3,11]

Figure 2 shows the high statistics Ps-fraction data measured at 500 K with typical fits in Mo(111). A conventional analysis with an exponential implantation profile ($m=1$) yields $n=1.63(2)$ and $L_+=(D_+\tau)^{1/2}=AE_0^n=800(30)$ Å with $\chi^2=1.8$. We notice that the exponential profile is not adequate to fit the data. A second fit with a Gaussian implantation profile ($m=2$) yields $n=1.19(3)$ and $L_+=360(15)$ Å with $\chi^2=1.24$. This is already more reasonable, but the parameter n is out of its experimental range 1.4—1.7. These two examples show that parameters m and n are correlated in the fitting routine, although they have a different physical origin. The same problem has also been observed in silicon.[7]

Experimental Ps-fraction data $f(E)$ may therefore contain a contribution, not only from thermalized positrons, but also from various fast escape processes, which result in formation of "hot" positronium.[1,18] In fact, we have observed[19] that *only* epithermal positrons can form Ps (up to 40% of incident positrons) from an annealed Cu(111) sample, containing a few monolayers of water at the surface. Therefore, the positronium fraction data analysis should be started from sufficiently high incident energies E, where the various hot Ps contributions have vanished.

The shape of the implantation profile was first verified by fixing n to a physically reasonable value $n=1.6$. The data was then analyzed as a function of the minimum incident energy E_{min} included in the fit. This run showed that the parameter m converged to $m=1.8(5)$ at high E_{min}. A second run was done with $m=2$. At $E_{min}<2.5$ keV n stayed at about 1.2, and thereafter it increased to 1.55(15). At $E_{min}>4$ keV errors in n were about 30%. Finally, n and m were fixed to 1.55 and 2.0, respectively. The results for E_0, $f(0)$, and χ^2 are given in Table I. It shows that E_0 increases as a function of E_{min} and then levels off at around $E_{min}=3.5$ keV. The corresponding χ^2 values level to $\chi^2=1.07(4)$. The fit at $E_{min}=4$ keV is shown in Fig. 2 (solid line), and it fits all data with $L_+=1100(30)$ Å. This result is also independent of the minimum fitted energy E_{min} above 4 keV.

From the above we conclude that various epithermal and backscattered positrons have a high probability to form hot Ps at the surface at $E<4$ keV. The difference

TABLE I. Fitted values of the diffusion parameter E_0, Ps fraction $f(0)$, and χ^2 are shown as a function of the minimum energy E_{min} included in fitting the high statistics Ps-fraction data $f(E)$ in Mo(111) at 500 K. Parameters m and n are fixed to 2 and 1.55, respectively.

E_{min}	E_0	$f(E)$	χ^2
0.5	6.25(6)	37.5(2)	3.64
1.0	6.41(6)	36.8(2)	3.00
1.5	6.7(1)	35.5(3)	2.12
2.0	6.8(1)	34.7(3)	1.79
2.5	7.1(1)	33.4(4)	1.36
3.0	7.3(1)	32.7(4)	1.17
3.5	7.5(1)	31.7(5)	1.05
4.0	7.5(2)	31.3(6)	1.06
4.5	7.7(2)	30.8(8)	1.05
5.0	7.6(2)	30.8(9)	1.08
5.5	7.5(2)	32.0(1)	1.15
6.0	7.3(3)	33.0(1)	1.06
6.5	7.1(3)	35.0(2)	1.03

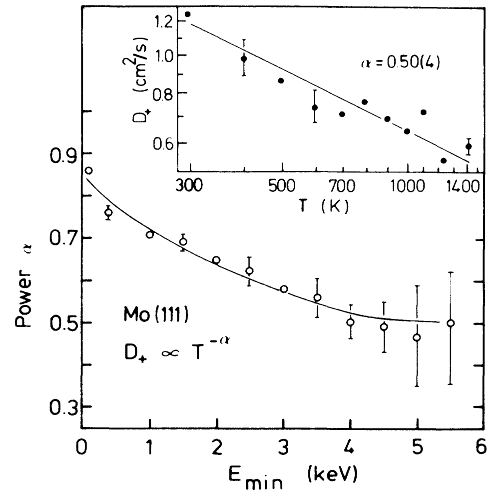

FIG. 3. The power α of the temperature dependence of the positron diffusion coefficient is shown as a function of the minimum energy E_{min} used in fitting Ps fraction data at different temperatures. α approaches the theoretical value $\alpha=\frac{1}{2}$ at $E_{min}\approx 3.5$ keV. The inset shows a least-squares fit for $D_+(T)=D_0T^{-\alpha}$ at $E_{min}=4$ keV.

between data points $f(E)$ and the solid line in Fig. 2, which we ascribe to hot Ps, is also shown in the figure (squares). The modeling of this curve is, however, not possible at the moment because the analysis involves diffusion properties of epithermal positrons, cross sections for hot Ps formation from different epithermal and backscattered positrons, and hot Ps detection efficiencies, which all may depend on the energy of nonthermal positrons. Therefore the data in Figs. 1 and 2 are not directly comparable with each other. The absolute fraction of hot Ps should be determined in a direct angular resolved time-of-flight or a 2D-ACAR measurement.

The data for all temperatures was analyzed with $m=2$ and $n=1.55$, using different values E_{min}. The resulting diffusion coefficients D_+ for each E_{min} and T were fitted to a $T^{-\alpha}$ power law. The results are shown in Fig. 3. The power α at $E_{min}=0.1$ keV is $\alpha=0.86(3)$ in accord with Schultz *et al.*[4] in Mo(110). When $E_{min}\approx 3.5$ keV, α approaches the theoretically predicted value $\alpha=\frac{1}{2}$. Within statistical accuracy $\alpha=0.5$ is valid up to $E_{min}=9$ keV with error bars increasing with E_{min}.

The inset in Fig. 3 shows the positron diffusion coefficient $D_+(T)$ at $E_{min}=4$ keV. A fit to the power law (solid line) yields $D_+(300\text{ K})=1.2(1)$ cm^2/s and $\alpha=0.50(4)$. In order to suppress the effect of the hot Ps fraction in Mo, we notice that the positron diffusion data $f(E)$ should be omitted, until the measured Ps fraction falls to about one half of $f(0)$. Our findings are in quantitative agreement with recent hot Ps measurements by Howell *et al.*[18]

The consequences of improper treatment of the experimental Ps fraction data are not limited to the temperature dependence of the positron diffusion coefficient. We strongly emphasize that all measurements based on either Ps or reemitted positron-fraction determination, and which include low incident positron energies, should be reanalyzed. Below we discuss some examples to illustrate that point.

Schultz *et al.*[4] have reported results where the diffusion length L_+ is reduced at low temperatures. This was attributed to positron localization into shallow traps both in annealed[4] and in neutron-irradiated[20] aluminum. At low temperatures positron slowing down is less effective, resulting a longer thermalization time.[14] Therefore, a higher fraction of the Ps signal is expected to be due to epithermal positrons. The extracted diffusion length L_+ is then artificially short, as data analysis includes low incident energies, and this effect is expected to be more prominent at low temperatures. Ps-fraction data has also been used to measure the vacancy formation energy in Al,[8] where an artificially high value was reported. The contribution of the hot Ps atoms should again be suppressed, because the positron mobility data is primarily coming from positrons implanted very close to the sample surface.[16]

The anomalous behavior of D_+ in Cd (Ref. 4) is reported to be due to the anisotropic nature of the crystal. It should be verified whether the positron slowing down properties, rather than the positron diffusion behavior, is more sensitive to crystal orientation.

In conclusion, we have observed that low-energy positrons injected into metallic samples have a high probability of escaping the sample surface prior to thermalization. The reemitted epithermal positrons have a distinct energy spectrum, with a maximum at about 0.5 eV above the elastic threshold. An excess hot Ps contribution is deduced from the analysis of the back-diffusion data. Suppressing this nonlinear contribution we show that (i) the positron implantation profile has a shape of a derivative of a Gaussian function, as suggested by simulation results, (ii) in contrast to recent experimental indications thermal positron diffusion at least in molybdenum seems to be dominated by acoustic phonon scattering, and (iii) all positron mobility measurements based on the determination of Ps or reemitted positron fraction should be reanalyzed. This will yield revised information on positron diffusion and trapping processes.

Note added. We have recently performed Ps fraction versus energy measurements in Ag(111) at 120–700 K. Similar data analysis yields for the temperature dependence of positron diffusion $\alpha = 0.60(17)$.

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*Present address: Laboratory of Applied Physics I, Technical University of Denmark, DK-2800 Lyngby, Denmark.

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