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Experimental support for physisorbed positronium at the surface of quartz

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We report temperature-dependent positronium (Ps) emission from a single crystal of SiO_2 using a monoenergetic positron beam. Slow positrons (e^+) from an electrostatic beam system were injected with variable energy (0–1600 eV) into the SiO_2 target and Ps emission from the target surface was studied as a function of incident e^+ energy (E) as well as target temperature (T). Our data suggest a physisorbed Ps surface state which is temperature activated into a "slow" Ps emission with an activation energy of ~ 0.15 eV. In addition, a large Ps yield (40% of the incident 400 eV positrons are emitted as Ps) is observed even for $T \rightarrow 0$ K, attributed to "fast" Ps produced by the bulk Ps formed within the SiO_2 target and diffusing to the surface. From the Ps yield vs E we find a bulk Ps diffusion constant of 0.047 ± 0.013 cm^2/sec. We also observe a slow e^+ reemission yield of (15 ± 2)% at 400-eV incident e^+ energy.

In the last few years variable energy (0–10 keV) positron (e^+) beams have been used to study the e^+ reemission and positronium (Ps) formation mechanisms from well-characterized metal surfaces.[1] When some of the implanted and thermalized positrons reach the metal surface by diffusion, several processes can occur: (a) positrons can be reemitted from the surface in the case of a negative work function, (b) positrons can capture an electron and leave as "fast" Ps (few eV), or (c) they can be trapped into a surface state that can be subsequently thermally activated into "slow" Ps emission. The exact nature of the surface state is presently being studied by angular correlation of 2γ annihilation radiation (ACAR) techniques.[2]

Much less is known about e^+ and Ps emission mechanisms from insulators: Ps emission has been studied from ice[3] and e^+ and Ps emission have been observed in some alkali halides, as well as in Al_2O_3 and SiO_2.[4] Unlike in metals, Ps can be formed in the bulk of insulators. A delocalized, excitoniclike Ps Bloch state has been observed by ACAR techniques in single crystals of quartz, ice, and some alkali halides.[5] Because of the importance of producing high-intensity Ps beams for various future experiments, the study of Ps emission from insulators is of great interest. The nature of the surface interaction of the bulk delocalized Ps as well as of delocalized positrons in insulators forms an interesting problem of its own.

In this Rapid Communication we report the first temperature-dependent Ps emission study from an insulator, in this case a quartz single crystal. From the dependence of the Ps yield on the incident e^+ energy we deduce a (bulk) Ps diffusion constant. In addition to Ps emission, we also observe slow e^+ emission.

The experiment was performed in a UHV system (10^{-10}-Torr range). A monoenergetic positron beam was electrostatically guided to the sample chamber where the annihilation quanta were measured by a 3-in. NaI(Tl) detector placed outside the vacuum chamber, 5 cm from the sample (Fig. 1). Slow positrons were obtained from a ^{58}Co source placed before a W(111) single-crystal moderator in the back-reflection geometry.[1] The W moderator was electropolished to a mirror finish and was annealed *in situ* at 1800 K under UHV conditions. The e^+ beam energy spread was measured to be ~ 1 eV full width at half maximum (FWHM); the fast to slow e^+ conversion efficiency was typically $\epsilon \sim 4 \times 10^{-4}$.

The sample was an AT cut, "Z-region," right-handed single crystal of synthetic quartz, 0.038 cm thick, supplied by the Sawyer Crystal Co., with an infrared quality factor[6] of $Q = 2.5 \times 10^6$. It was mechanically polished with cerium oxide polishing compound and chemically etched in a 6% HF solution at 50 C for 40 sec. Auger spectroscopy and argon sputtering were used to characterize the surface composition and to remove contamination.

Since the amount of bulk Ps formed in quartz is strongly dependent on the quality of the sample, we used the Brandeis two-dimensional (2D) ACAR system[2] to obtain the intensity of the bulk Ps in our sample. The presence of "umklapp" Ps peaks[5] confirmed the production of delocalized Ps; we obtained an ≈ 5% intensity narrow ACAR component (central peak plus umklapp components), consistent with typical results for high-purity quartz.

The quartz sample was part of the retarding element of a retarding field analyzer (RFA), Fig. 1. By varying the voltage V_R, we were able to change the incident e^+ energy E and eventually turn the e^+ beam around. By monitoring in time the turnaround voltage, we estimated (to within ~ 1 eV) the amount of charging of the sample for various temperatures. Below 600 K charging of 5–10 V was observed.

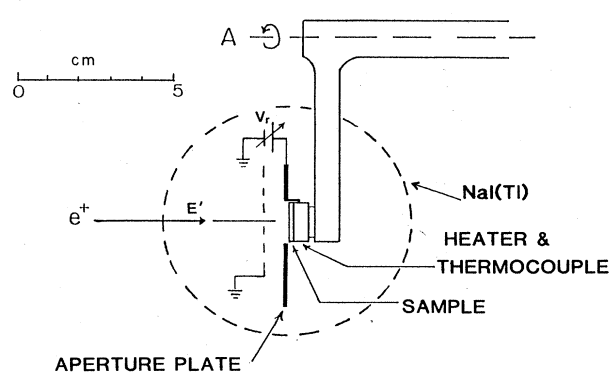

FIG. 1. Sample chamber with the retarding field analyzer (RFA) and the NaI(Tl) detector placed 5 cm away from the sample. The final energy of the positrons is $E = E' - V_R$.

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No charging was detectable above 600 K; we were thus assured that the temperature effects observed above 600 K were not associated with charging of the quartz sample. In the Ps emission studies the incident e^+ energy was changed with a set of electrostatic zoom lenses in order to hold the sample bias V_R constant.

We found that Ps as well as positrons were emitted when the quartz sample was bombarded with the monoenergetic e^+ beam. In metals, the Ps yield Y_{Ps} from the surface depends on the e^+ incident energy E as well as on the temperature T of the sample. Because of our weak ^{58}Co source, we did not measure the full two dimensional $Y_{Ps}(E,T)$ surface; instead, we obtained $Y_{Ps}(E)$ at the fixed temperature of 600 K and $Y_{Ps}(T)$ for $E=400$ eV and $E=1600$ eV. The Ps emission yield was obtained in the standard way using peak-to-valley ratios deduced from NaI(Tl) spectra.[1] The NaI(Tl) detector was calibrated by using a ^{68}Ge source encapsulated in a metal sandwich for the "no Ps" case, and a 50-eV as well as a 400-eV positron beam on a Cu(100) sample heated to 1200 K for the 100% Ps case. Systematic errors due to the calibration were estimated to be 5–10%. The o-Ps signal from bulk annihilation was estimated to be less than 1%.

In order to test for e^+ emission, we have alternately biased the sample +50 and −50 V. The observed Ps yield versus incident positron energy E is shown in Fig. 2. We notice that there is clear evidence for e^+ reemission and/or inelastic e^+ backscattering from the sample; below $E\sim 400$-eV incident e^+ energy the Ps yield shows an increased difference between the +50- and −50-V runs as $E\rightarrow 0$. In order to obtain the energy distribution of these positrons, we set up a NaI(Tl) telescope to measure the 2γ coincidence yield from the target area as a function of V_R, at an incident positron kinetic energy of $E'=400$ eV. We have measured this yield from $V_R=-50$ V to $V_R=+500$ eV, and obtained a slow e^+ beam yield of 0.15(2) per incident e^+, with a mean energy of $\sim$0–2 eV and a high-energy tail extending to $\sim$10 eV. In addition, we find a broad distribution of inelastically scattered positrons of an intensity of approximately 0.25(5) per incident e^+, extrapolated to $E=E'-V_R\simeq 0$ incident e^+ energy; this inelastic yield approaches zero as $V_R\rightarrow 0$, i.e., $E\rightarrow 400$ eV.

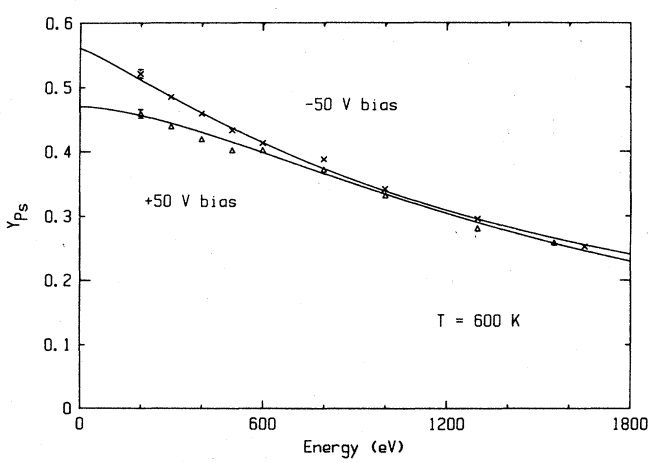

FIG. 2. Fraction of Ps emitted per incident positron vs energy. ×: −50-V bias; Δ: +50-V bias. The curves are fitted using a 1D diffusion model.

Using the usual 1D diffusion model[1] and an exponential e^+ implantation profile with a mean implantation depth of $\bar{x}=AE^n$, one obtains for the Ps yield[1] (i.e., the fraction of Ps per incident e^+):

$$Y_{Ps}=Y_0/[1+(E/E_0)^n] \quad , \tag{1}$$

where $AE_0^n=\sqrt{D\tau}$, D being the diffusion constant of the diffusing species, τ its lifetime, and A a parameter dependent only on the density ρ of the target[7] and given by $A=4/\rho$ μg/cm^2/(keV)^n. Fitting Eq. (1) to the −50-V bias run (Fig. 2), we obtain $E_0=1425(60)$, $Y_0=0.56(2)$, $n=1.2(1)$ with $\chi^2/\nu=1.2$; with the +50-V bias, we obtain $E_0=1750(60)$, $Y_0=0.47(1)$, $n=1.6(2)$ and $\chi^2/\nu=1.6$. Given, however, the uncertainty in the inelastically backscattered e^+ beam spectrum, the physical meaning of such an estimate is doubtful. The safest estimate of the E_0 responsible for Ps emission is to fit Eq. (1) to the $Y_{Ps}(E)$ data only for $E\geqslant 500$ eV, where we find the effect of inelastic backscattering to be small. Such a fit gives us $E_0=1700(60)$, $Y_0=0.49(2)$, $n=1.6(2)$, and $\chi^2/\nu=0.8$ for the −50-V and $E_0=1800(50)$, $Y_0=0.44(2)$, $n=1.9(2)$ and $\chi^2/\nu=2$ for the +50-V data. We note that these later constants are in essential agreement with the +50-V fit using the full energy range.

We do not know *a priori* if the Ps emitted from the surface of quartz is formed by the bulk delocalized Ps diffusing to the surface, by the bulk thermalized positrons, or by a combination of both. In principle, Ps formation by thermalized positrons reaching the surface (as in the case of metals) is energetically unfavorable, since the ionization energy of quartz is $\sim$10 eV. There is the possibility of the Ps formation with "spur electrons"[8] (i.e., with electrons produced during the e^+ slowing-down process), if such "spur electrons" are copiously present at the surface of quartz. We feel, however, that it is more likely that the observed Ps emission is due mainly to bulk Ps diffusing to the surface. From our estimate of $E_0\sim 1700$ eV, we obtain the bulk Ps diffusion constant of $D=0.047(13)$ cm^2/sec, using the measured[9] o-Ps lifetime (due to "pick-off") of $\tau=2.76\times 10^{-10}$ S. This value is much smaller than the typical value for positrons in metals[1] and is a factor of 6 lower than the one estimated by Dupasquier[5] derived from the ACAR data of Ikari and Fujiwara,[10] but still a factor of $\sim 10^3$ larger than D obtained from SiO_2 amorphous powder experiments.[5] As Mills and Crane[4] point out, this could be due to partial self-trapping of Ps. Besides the data of Fig. 2, we have also obtained some preliminary data at low e^+ incident energies ($E\leqslant 50$ eV) and find oscillations in the Ps yield similar to those obtained for ice,[3] albeit with a much smaller amplitude. Such oscillations might be evidence for an Ore gap mechanism of Ps formation as discussed by Eldrup, Vehanen, Schultz, and Lynn.[3]

Figure 3 shows the Ps emission yield observed as a function of temperature. We show three separate results: $Y_{Ps}(T)$ at 400-eV incident e^+ energy from a surface showing a carbon surface contamination of $\gtrsim 50\%$ and $Y_{Ps}(T)$ at 400- and at 1600-V e^+ energy from a surface that was cleaned by sputtering to a carbon surface contamination of $\lesssim 10\%$. The sample was biased negatively; runs taken with a positive bias, however, yielded an identical T dependence. Most of the data was obtained cycling the temperature from room to high and back to low temperature. Some hysterisis

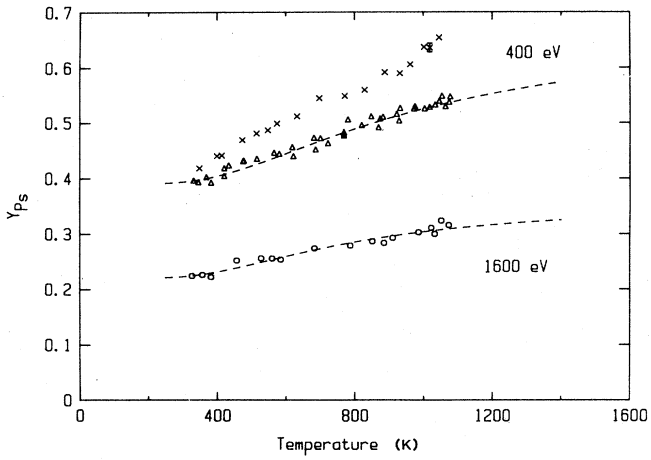

FIG. 3. Fraction of Ps emitted per incident positron vs temperature. ×: $E=400$ eV, $>50\%$ C; Δ: $E=400$ eV, $<10\%$ C; ○: $E=1600$, $<10\%$ C. The fitted curves are derived from a one-step temperature-activated model.

was present below 750 K. The lower-temperature Ps emission fractions would gradually (a few hours) return to the initial ones. Starting at 600 K, instead of at room temperature, was sufficient to avoid hysterisis in the low-temperature region. This fact could be related to a possible slow charging of the sample at lower T or to contamination. To check the latter possibility we took various Auger spectra at different T. No change was detected above the 1% level. Probably the charging has a very small effect on the charge-capture processes, but serious defocusing of the beam due to spurious fields could introduce systematic errors, which can explain the small hysterisis observed ($<10\%$). The data points in Fig. 3 were all taken from high to low temperature.

In ACAR studies of quartz, Ikari and Fujiwara[10] found that the Ps peaks survive at least up to 700 K, and the para-Ps intensity increases with T at low temperatures, but levels off above 500 K. From this, we conclude that our observed temperature effect (Fig. 3) cannot be due to a temperature-dependent bulk Ps formation probability, since it extends from 400 to 1200 K. Fitting straight lines to the clean sample runs ($<10\%$ C) yielded a χ^2/ν of 1.4 for the 400- and 1600-eV incident e^+ energy data; the fractional increases with increasing T relative to the zero-T intercepts were found to be the same for the two energies. Since the implantation depth at 400 and 1600 eV differ by a factor of 9, this observation indicates strongly that the observed temperature effect is associated with a surface process; the difference between the two energies simply reflects the ratio of the bulk Ps diffusing to the surface.

If the temperature-activation process at the surface is a one-step process, the temperature dependence of the Ps yield should exhibit the usual Arrhenius (S) shape. Unfortunately, we could not lower the temperature below 400–500 K due to the charging effect, and could not increase the temperature above 1200 K because of limitations in the target assembly design. Although there is a lack of clear asymptotic $T\rightarrow 0$ and $T\rightarrow\infty$ behavior in the data, an estimate of the activation energy can still be obtained from the data. We fit the usual one-step temperature-activation model formula,[1]

$$Y_{Ps}(T)=\frac{BY_{Ps}(\infty)+Y_{Ps}(0)}{1+B}\ , \tag{2}$$

where $B=(\nu_0/\lambda_s)e^{-Ea/kT}$, and $Y_{Ps}(\infty)$ and $Y_{Ps}(0)$ are the Ps yields at $T\rightarrow\infty$ and $T\rightarrow 0$. The large uncertainty in estimating $Y_{Ps}(\infty)$ and $Y_{Ps}(0)$ discouraged us from trying a temperature-dependent[11] ν_0 fit; such a dependence would not have, however, a large effect on the activation energy. The fit leads to large uncertainties in estimating ν_0/λ_s, but less for E_a. We obtain $Y_{Ps}(\infty)=(0.7-0.9)$, $Y_{Ps}(0)=0.4$, and $E_a=(0.14\text{–}0.17)$ eV, with a χ^2/ν of ~ 1.7. This activation energy is 2–5 times smaller than that obtained for metals. In addition, the fitted value of (ν_0/λ_s) is $\sim 3\text{–}10$, which is over 30 times lower than the corresponding values observed for chemisorbed Ps desorption from metals. Chemisorbed Ps is equivalent to the positron correlation potential surface state, and requires a Ps activation energy of

$$E_a=E_b+\phi_- -6.8\text{ eV}\ , \tag{3}$$

where E_b and ϕ_- are the positron surface-state binding energy and electron work function, respectively.[1] Applying this picture to quartz would yield an E_a value much higher than our measured value, since $\phi_-=10$ eV, and $E_b\approx 1$ eV is a reasonable estimate for a positron in the image potential of a highly polarizable material. Alternatively, we would expect a physisorbed Ps atom in a Van Der Waals–type image potential[12] to have a much smaller value of E_a. Also, the simple intuitive picture of the frequency prefactor ν_0 corresponding to the classical oscillation frequency of a bound particle in its surface potential suggests that our thermal-activation data corresponds to the desorption of physisorbed Ps. The speculation that we are observing a physisorbed Ps surface state must be tempered with the possibility that there are electrons near the surface that are bound to the quartz with energies appreciably less than ϕ_-. This would allow a positron in a surface state to capture an electron and leave the surface as Ps with a much smaller E_a than that given by Eq. (3). A more rigorous examination of the physical significance of ν_0 is also warranted.

In order to check our assumption that the observed Ps emission is mainly due to bulk Ps, we estimate the total bulk Ps available in quartz. From magnetic quenching experiments Greenberger, Mills, Thompson, and Berko[13] have estimated an "electron density parameter"[5] of $(1/1.4)^3$ for Ps in quartz, i.e., an effective "natural" decay rate of para-Ps of 2.7 nsec^{-1}. This means that para-Ps decays with a 2.7-nsec^{-1} rate via the "narrow ACAR peaks" channel and with a 3.6 nsec^{-1} rate by pick off into a broad ACAR component. Given, therefore, $\sim 5\%$ narrow ACAR peak annihiltion, one estimates the total bulk Ps formation yield to be $\sim 47\%$. This value is of the right order to account for $Y_{Ps}(0)$, i.e., the fraction that is not activated thermally; we assume that $Y_{Ps}(0)$ corresponds to "fast" Ps (few eV) emission. If the thermal-activation model is correct, we have to account for at least an additional 30%–40% trapped at the surface that can be thermally activated into slow Ps. It therefore seems more probable that the surface state is not formed by bulk Ps, but by Bloch state positrons diffusing to the surface, and forming Ps at or near the surface with impurity electrons or spur electrons.[8] The same positrons are responsible for slow e^+ emission.

To recapitulate our yield measurements: At 400-eV in-

cident e^+ energy, with the sample held at 400 K, 15% of all positrons are reemitted as a slow e^+ beam, 40% are reemitted as Ps, and 10% annihilate in the bulk (according to $E_0 \simeq 1700$). The remaining 35% are, therefore, bound to the surface, possibly as physisorbed Ps, and can be thermally activated with an activation energy of ~ 0.15 eV.

We are presently carrying out a program of measuring the velocity and angular distribution of the thermally and nonthermally activated Ps emission. This will provide important additional information on Ps formation and emission from quartz as well as investigate the possibility of using this process as a source of Ps for high-precision QED measurements.[14]

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[1]See the review by A. P. Mills, Jr., in *Proceedings of the International School of Physics "Enrico Fermi," Course LXXXIII,* edited by W. Brandt and A. Dupasquier (Academic, New York, 1982), and references therein.

[2]R. H. Howell, P. Meyer, I. J. Rosenberg, and M. J. Fluss, Phys. Rev. Lett. **54**, 1698 (1985); K. G. Lynn, A. P. Mills, Jr., R. N. West, S. Berko, K. F. Canter, and L. O. Roellig, Phys. Rev. Lett. **54**, 1702 (1985); for the ACAR technique, see the review by S. Berko in Ref. 1, and references therein.

[3]M. Eldrup, A. Vehanen, P. J. Schultz, and K. G. Lynn, Phys. Rev. Lett. **51**, 2007 (1983).

[4]A. P. Mills and W. S. Crane, Phys. Rev. Lett. **53**, 2165 (1984).

[5]See the review by A. Dupasquier in Ref. 1 and references therein.

[6]J. C. Brice, Rev. Mod. Phys. **57**, 105 (1985).

[7]S. Valkealahti and R. M. Nieminen, Appl. Phys. A **32**, 95 (1983).

[8]O. Mogensen, J. Chem. Phys. **60**, 998 (1974).

[9]C. H. Hodges, B. T. A. McKee, W. Triftshauser, and A. T. Stewart, Can. J. Phys. **50**, 103 (1972).

[10]H. Ikari and K. Fujiwara, J. Phys. Soc. Jpn. **46**, 92 (1979).

[11]S. Chu, A. P. Mills, Jr., and C. A. Murray, Phys. Rev. B **23**, 2060 (1981).

[12]S. M. Kim and W. J. L. Buyers, J. Phys. C **11**, 101 (1978).

[13]A. Greenberger, A. P. Mills, Jr., A. Thompson, and S. Berko, Phys. Lett. **32A**, 72 (1970).

[14]S. Berko and H. N. Pendleton, Annu. Rev. Nucl. Part. Sci. **30**, 543 (1980).