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Electron emission due to positronium annihilation in solid Ar, Kr, and Xe

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We present measurements of positron and electron emission by solid rare-gas surfaces implanted with low-energy positrons. The electron yield exhibits a 0.5-eV-wide peak at a positron energy just above the threshold for positronium (Ps) formation, but below the electron-hole–pair threshold. A similar peak in the fraction of the incident positrons annihilating in the sample leads us to conclude that (1) slow Ps has an anomalously short diffusion length possibly due to self-trapping, and (2) energetic electrons are liberated from Ps atoms following annihilation of the positrons with valence electrons. The energy spectrum of the emitted electrons should contain information about the internal Ps wave function in the solids.

The dynamics of positrons and positronium (Ps) in insulators has many similarities to that of electrons and excitons. The two-body problem of the Ps or exciton bound state is complicated by the inseparability of the relative and center-of-mass (c.m.) coordinates in an external potential. Information about the c.m. momentum distribution of Ps may be obtained from an angular correlation of annihilation radiation (ACAR) study of its self-annihilation γ rays. For example, in the alkali halides, ACAR experiments have shown that the Ps can exist in either a delocalized Bloch state or in a metastable localized self-trapped state.[1] Complementary information about the relative electron-positron wave function could be obtained if we could collect and measure the energy of the Ps electrons remaining after the positron annihilates with an electron of the solid. We have obtained evidence for the emission of Ps electrons from solid Ar, Kr, and Xe, and identified the electrons by their occurrence in association with an anomalously short Ps diffusion length at low energies. Whether the Ps is actually self-trapped or not, we now have an opportunity for examining new details of its state in a simple solid through energy measurements on the emitted electrons.

Our experiment began as an attempt to determine the threshold energy for electron-hole–pair formation by positrons in the rare-gas solids. Ar, Kr, and Xe samples were prepared by freezing onto a cold finger, and bombarded with slow positrons of variable energy. Electrons excited by the positron irradiation and ejected from the surface were collected by a channeltron in a manner similar to our earlier experiments.[2] We expected to see a sharp onset in the electron yield at a positron energy equal to the gap energy E_g plus the electron affinity E_a if it is greater than zero, and minus the positron work function ϕ_+. Unfortunately, the measurement could not be made very precisely because of a disappointingly slow rate of increase in the electron yield at the thresholds, indicated by the arrows (↓) in Fig. 1. However, 2 or 3 eV below the threshold the electron yield exhibits an unexpected sharp peak which immediately became the object of study.

To discover the origin of the new peak, we repeated some of our earlier measurements on positron inelastic thresholds on the same sample for which the electron yield was determined. As described in detail in Ref. 2, our measurements were performed on a magnetically guided positron beam in an ultrahigh-vacuum system. The Ps yield was determined from the two-photon and

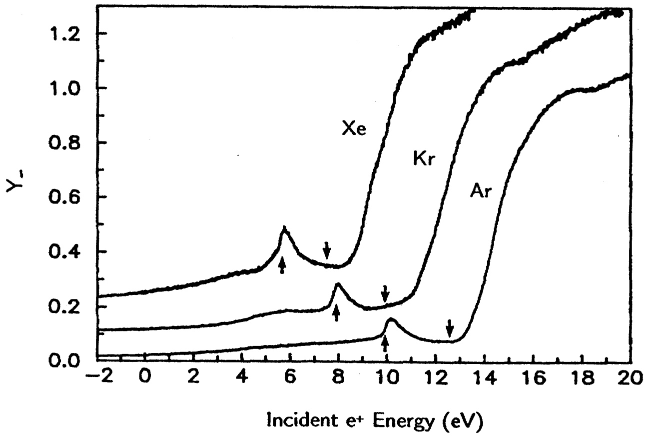

FIG. 1. Electron-emission yield for Ar, Kr, and Xe surfaces implanted with slow positrons with energy up to 20 eV. The curves have been normalized to 1 at the knee above the electron-hole–pair threshold. To within ±30%, the vertical scale is electrons emitted per incident positron. The Xe and Kr curves are displaced vertically by 0.2 and 0.1, respectively. The positron inelastic thresholds (↑) and electron-emission thresholds (↓) are indicated. The zero of energy is taken to be the minimum positron energy for which annihilations at the target surface are observed.

three-photon annihilation yields measured with a NaI(Tl) scintillation counter.[3] The positron- and electron-emission yields were measured using a channel electron multiplier biased appropriately in consecutive runs. Figure 2 shows the electron yield per incident positron, Y_-, and the positron elastic backreflection coefficient[4] R_+, in the vicinity of the electron peak for an Ar sample, before and after annealing. It is evident that within the 0.03-eV resolution of our instrument the electron peak commences at precisely the energy that we have associated with the positron inelastic threshold.[2]

In Fig. 3 we show the fraction of positrons, again for solid Ar, as a function of the incident energy, which (a) are reemitted as free positrons (Y_+), (b) are emitted as Ps ($Y_{\rm Ps}$), and (c) annihilate with an electron in the sample (Y_s). (a) and (b) of Fig. 3 are in agreement with our earlier measurements,[2] while (c) is new. Note that since the sum of the three yields must equal unity, $Y_+ + Y_{\rm Ps} + Y_s = 1$, Y_s is in principle redundant. Nevertheless, the new effect that we are reporting here was missed in our earlier study[2] because Y_s was not displayed explicitly.

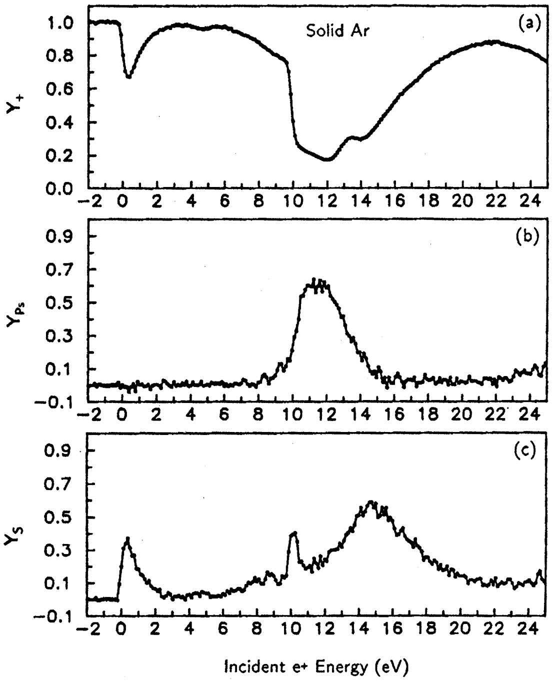

FIG. 3. Energy dependences of the probabilities for (a) positron reemission, (b) positronium emission, and (c) positron annihilation in the solid. The sample is a solid Ar surface.

We have already shown in Ref. 2 that a dip in Y_+ (and a corresponding peak in Y_s) near zero energy is explained by positrons becoming trapped in the sample due to the positive affinity, $\phi_+ = 1.55$ eV,[5] of solid Ar for positrons. The next feature in Fig. 3 occurs at an energy $E_{\rm th} = 9.9$ eV: Y_+ shows a sudden decrease, $Y_{\rm Ps}$ begins to rise, and Y_s has a narrow peak reminiscent of the peak in Y_-. We identify $E_{\rm th}$ with the threshold for the lowest electronic excitation in the solid containing one positron. Three possible excitations[6] with their threshold energies are (1) Ps formation, $E_{\rm Ps} - \phi_+$, (2) exciton creation, $E_x - \phi_+$, and (3) electron-hole–pair creation, $E_g - \phi_+$. The thresholds for the last two processes may be calculated from photoabsorption measurements[7] and the recently measured positron work function.[5] They are found to be $E_x - \phi_+ = 10.51$ eV and $E_g - \phi_+ = 12.60$ eV. Since $E_{\rm th}$ lies below both of these thresholds, we conclude that $E_{\rm th}$ corresponds to the threshold for producing Ps in solid Ar. The small shoulder in $Y_{\rm Ps}$ with a threshold at about 8 eV is attributed to Ps forming outside the surface due to the presence of contaminants. The shoulder was observed to increase with time as would be expected for an effect caused by the condensation of background gas on the sample surface. From the measured value of the Ps threshold, we may determine the Ps work function ϕ_{Ps}, which is the difference in energy for Ps in vacuum and Ps inside the solid. Using the measured band gap and electron affinity of solid Ar we obtain $\phi_{\rm Ps} = E_g + E_a - \frac{1}{2}R_\infty - E_{\rm th} = -2.6 \pm 0.1$ eV, in agreement with our previous determination.[2] A decrease in $Y_{\rm Ps}$ starting at about 12 eV is still below $E_g - \phi_+$ and therefore must be due to exciton creation.

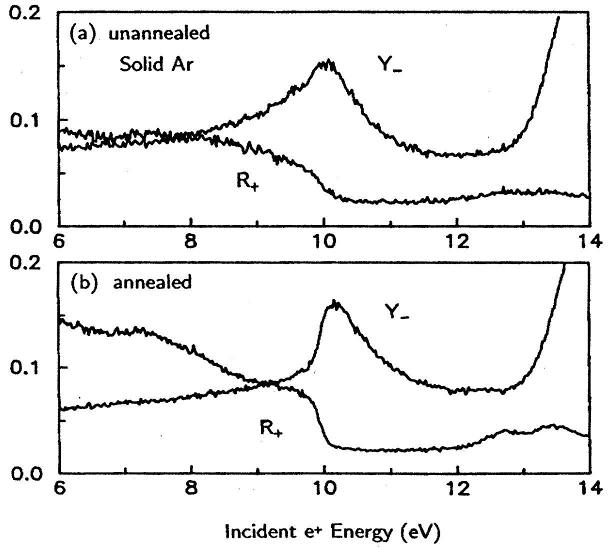

FIG. 2. Detail of the narrow energy electron peak from Fig. 1 for (a) unannealed Ar, and (b) annealed Ar. The positron reflection coefficient R_+ is superimposed.

The peak in Y_s which occurs at the Ps formation threshold in Fig. 3(c) is clearly much narrower than the peak in $Y_{\rm Ps}$ and must result from ortho-Ps or free positrons that annihilate in the solid. (Our measurements are insensitive to para-Ps since it annihilates into two photons both inside the sample and in vacuum.) Since the peak occurs below any other thresholds, it must be due to Ps and we can offer only two explanations for its existence: (1) Ps is more efficiently trapped when it is formed with low kinetic energy, or (2) as the energy is increased above $E_{\rm th}$, the Ps is formed closer to the surface so that it can escape more easily. Either of these hypotheses make it likely that the electron peaks of Figs. 1 and 2 result from Ps which annihilates in the solid by pickoff with a valence electron. Following annihilation, the Ps electron will be left with about half the Ps binding energy, and emission of the electron will be likely, due to the long escape depth of hot electrons in the solid rare gases.[8]

We have attempted to model the peaks in Y_s and Y_- using a Monte Carlo simulation. Positrons were started at the surface of a thick film with energy E and momentum directed into the film. The probability of traveling a distance x without experiencing a collision was assumed to be $\exp(-x/l_t)$, where $1/l_t = 1/l + 1/l_{\text{Ps}}$, l_t is the total mean free path, l is the positron-phonon mean free path, and l_{Ps} is the mean free path for Ps formation. When a collision occurred, Ps was formed with a probability l_t/l_{Ps}; otherwise, quasielastic scattering occurred with energy loss $\delta E = 6$ meV (Ref. 2) and the direction of the positron's momentum was randomized. Ps formed at a depth x was assumed to escape from the solid with a probability $\exp(-x/l_{\text{esc}})$. As an estimate of Y_s, we calculated the fraction of incident positrons which resulted in the formation of Ps atoms that do not escape. We assumed $l = 50$ Å, independent of energy.[9] We estimated l_{Ps} from measurements of the Ps formation cross section, Q_{Ps}, in the gas.[10] We assumed a linear increase in Q_{Ps} with energy above the threshold. The calculations show that Ps forms at an average depth l just at threshold, and at shallower depths as Q_{Ps} increases. We find that the height of the Y_s peak depends mainly on l_{esc}, while the width is determined by the slope dQ_{Ps}/dE. In Fig. 4 the calculated Y_s (folded with a Gaussian of 0.2 eV full width at half maximum to simulate the experimental resolution) is compared with the measurement. A satisfactory agreement with the shapes of both the Y_s and Y_- peaks and the amplitude of the Y_s peak is obtained with the parameter values $l_{\text{esc}} = 100$ Å and $l_{\text{Ps}} = (10 \text{ eV Å})/(E - E_{\text{th}})$. The latter implies a dQ_{Ps}/dE consistent with Ref. 10, if we take into account their energy resolution and the reduced Ps binding energy in solid Ar relative to its vacuum value.

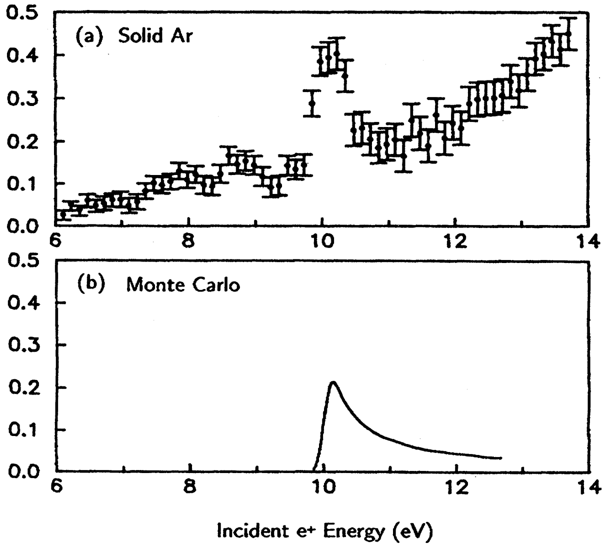

FIG. 4. Comparison of (a) the narrow peak in Y_s with (b) a Monte Carlo simulation using the parameters $l = 50$ Å, $l_{\text{esc}} = 100$ Å, and $l_{\text{Ps}} = (10 \text{ eV Å})/(E - E_{\text{th}})$.

It is thus apparent that the peak in Y_s can be explained by the rapid increase in Q_{Ps} above the threshold, provided the Ps diffusion length l_{esc} is short. The measured ortho-Ps lifetime would imply a Ps diffusion coefficient of order 10^{-3} cm^2 sec^{-1}, which would argue against the Ps being in a Bloch state. We may eliminate one possible reason for a small Ps diffusion coefficient by turning back to Fig. 2 and examining the effects of annealing. Since the amplitude of the peak in Y_- is independent of annealing, it would not appear that the Ps is trapping at defects.

Another possibility is the self-trapping of Ps. Indeed, excitons are observed to self-trap in all of the rare-gas solids.[7] Ps has been observed to self-trap in a bubble or cavity in liquid and solid He (Ref. 11) and in all the heavier rare-gas liquids.[12] An estimate of the energy of Ps in a cavity following Cohen and Jortner[13] shows that cavity formation would reduce the energy by between 0.8 eV for Xe to 1.6 eV for Ne. A self-trapped Ps state should therefore be stable in the rare-gas solids.

The long ortho-Ps lifetime in the rare-gas solids (2.5 nsec in solid Ar at 84 K) has been attributed to trapping of the Ps in large voids.[14] Although defects are expected for films grown from the vapor at low temperatures, the long lifetime is found in solid Ar at even a few degrees below the triple point where there should be no voids. ACAR measurements on solid Ar, Kr, and Xe which show no evidence of a narrow Ps self-annihilation peak[12] do not necessarily preclude cavity formation, because (1) the Ps zero-point energy might make the peak too broad to observe, and (2) Ps might not thermalize in less than the few-hundred-psec para-Ps lifetime. Indeed, long thermalization times might be expected by analogy with measurements on electrons in the rare-gas solids.[15]

Since anomalous self-trapping of Ps has been observed in the alkali halides,[16] it is natural to see if there is also a peak in Y_s for these materials. Measurements of Y_+, Y_{Ps}, and Y_s for KCl show that the Ps threshold is at 4.7±0.2 eV. We find a small shoulder on the Y_s curve near the threshold which could be due to self-trapped Ps. However, there is no sharp feature as was observed in the rare-gas solids. Further experiments are required since a 0.5-eV resolution may be obscuring the peak.

In conclusion, we have observed electrons which are emitted at the Ps formation threshold in solid Ar, Kr, and Xe. We have identified the electrons as Ps fragments liberated by slow Ps pickoff annihilation with valence electrons. It seems likely that the slow Ps is self-trapped by the formation of a cavity, since this is energetically favorable in all the rare-gas solids. However, it is clear that more measurements are needed. ACAR studies with a magnetic field to cause 2γ annihilation of the thermalized ortho-Ps would be useful, since the width of the

ACAR peak would tell us the radius of the cavity if it exists. Measurements of the Ps yield at higher incident positron energies should show that the Ps diffusion length is relatively short in contrast with the long diffusion lengths observed for positrons. Measurements of the emitted Ps velocity distribution would provide an interesting test since our prediction would be that only hot Ps will be able to escape from the rare-gas solids. A measurement of the energy distribution of the emitted electrons should yield information on the Ps internal wave function, particularly if performed on the rare-gas solids where the electrons may escape with little energy loss.

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