Angle-Resolved Positronium Emission Spectroscopy

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The momentum distribution of the positronium (Ps) emitted from an Al(100) surface being bombarded by low-energy positrons shows anisotropic lobes that gradually disappear as the initially clean surface is exposed to small amounts of oxygen. A clean Al(111) surface yields a more isotropic spectrum. The simplest model suggests that the anisotropy stems from the energy gaps in the projected nearly-free-electron band structure of Al. We conclude that inelastic many-body effects are weak and that the Ps spectra reflect the electron density of states near the surface.

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The various means of removing single electrons from matter can be useful probes of electronic structure if many-body final-state effects such as shakeup and multiple scattering can be understood or neglected. Photoemission,[1] Compton scattering,[2] and positron annihilation[3] are examples of interactions that primarily leave a solid in a one-hole excited state, and thus allow interpretation via a single-particle picture.[4] The emission into the vacuum of the positron-electron atom, positronium, is another means for removing a single electron from a solid. Since positronium (Ps) cannot exist inside a metal because of screening,[5] its formation should have a surface sensitivity similar to that of metastable atom deexcitation or ion neutralization.[4,6] However, Ps formation in principle contains more information because the light Ps mass allows the recoiling Ps momentum to be measured by time of flight[7] or by the angular correlation of its annihilation photons.[8,9] It has thus been suggested that Ps-velocity spectroscopy might be a good probe of the electronic density of states near the surface of a solid.[7] Verification of this suggestion requires showing that the Ps spectrum is not dominated by shakeup or other inelastic effects.

When a solid is bombarded by slow positrons in ultrahigh vacuum, three surface-related phenomena can be observed[3]: Some of the thermalized positrons diffusing from the bulk to the surface are ejected into the vacuum if the positron work function is negative, some are captured into a surface state, and some take part in Ps formation and emission. The maximum Ps emission energy is the negative of the Ps work function, given by the Ps binding energy in vacuum, $\frac{1}{2} R_\infty$, less the sum of the electron and positron work functions: $-\phi_{Ps} = \frac{1}{2} R_\infty - \phi_- - \phi_+$. The Ps time-of-flight experiments[7] showed that in Al the forward-emitted Ps is formed sufficiently free of inelastic effects to reveal the cutoff in the electron energy distribution at the Fermi surface. Subsequent observations of the Ps momentum distribution[8,9] by the angular correlation of annihilation radiation (ACAR) technique[3] were similar to the predictions of a simple theory for electron pickup,[7,10] but exhibited an isotropic shape that leaves open the possibility of many-particle final states. In this paper we show that Ps momentum distributions obtained with improved resolution and statistics are in fact anisotropic and reflect qualitatively the one-electron density of states. Ps emission is therefore not totally contaminated by shakeup effects, and could be an interesting surface-sensitive complement to angle-resolved photoemission.

Our experiment used slow positrons from self-moderated 12.8-h (half-life) ^{64}Cu sources[11] which gave a beam of maximum intensity $5 \times 10^7 \, e^+ \, sec^{-1}$. The positrons were magnetically guided to an ultrahigh-vacuum target chamber located between two Anger cameras. The increased beam intensity since our previous experiment[9] permitted an increased camera-to-sample distance of 11 m which resulted in an improved angular resolution of 1 mrad at an initial total coincidence counting rate of $\approx 20 \, sec^{-1}$. The positron beam energy was chosen to be 1.5 keV, small enough to allow the majority (70%) of the incident positrons to diffuse back to an Al surface, but large enough to reduce the number of nonthermal positrons at the surface to an insignificant level.[12] We selected Al for study because of its simple nearly-free-electron band structure and because it has been studied in detail.[1,13,14] The single-crystal samples were polished 1.5-mm-thick by 10-mm-diam disks oriented within 2° of the (100) or (111) direction. After preparation by sputtering with 1-keV Ar^+ ions and annealing, the surfaces produced sharp LEED patterns. Auger analysis showed that the initial surface impurities are <0.02 monolayer (ML) of C and O.
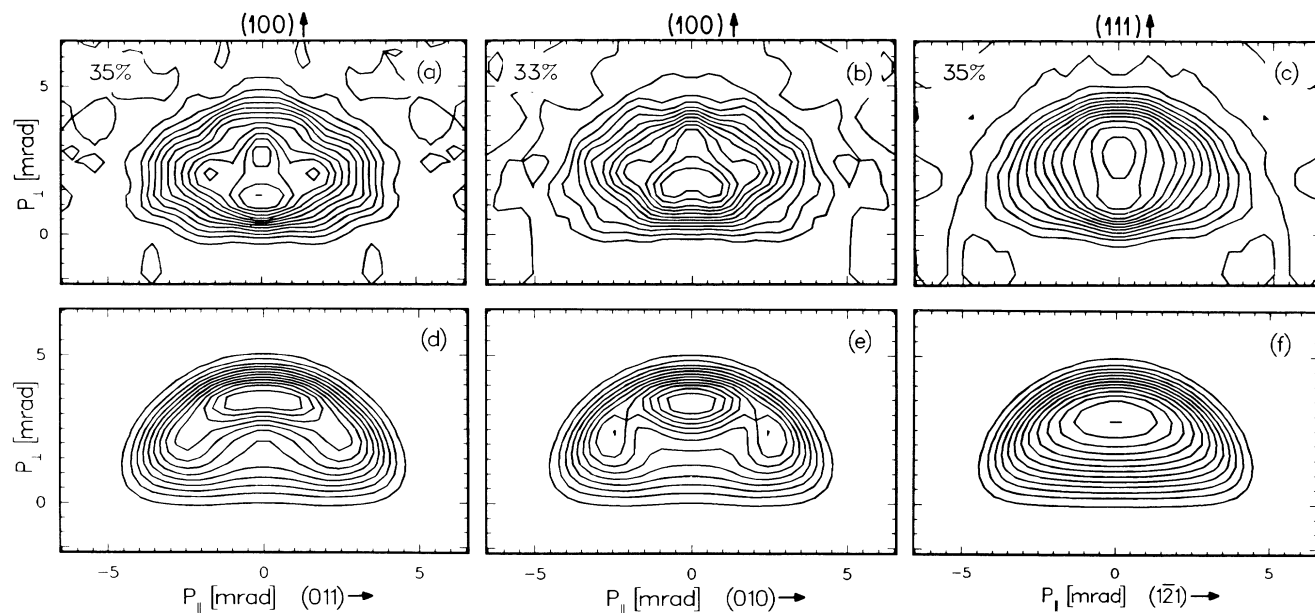
FIG. 1. 2D projections of the Ps-emission momentum spectra. Experimental results for (a) clean Al(100) surface, (b) same rotated 45°, (c) clean Al(111); and nearly-free-electron model for (d) Al(100), (e) Al(100) rotated 45°, and (f) Al(111). Each graph was made to have twelve contours above the zero level. The total number of counts in each spectrum is $\approx 4 \times 10^4$.

One-quarter of the Ps emitted is in the singlet state which annihilates into two 511-keV photons with zero total momentum in the Ps center-of-mass frame. The Anger cameras measure the directions of the two photons corresponding to two components of the Ps momentum, $p_\parallel$ and $p_\perp$. The third component, $p'_\parallel$, is integrated by the 2D ACAR yielding the 2D projection of the 3D Ps momentum density. The small distance moved by the singlet Ps in its 10^{-10}-sec lifetime is negligible. Since the emitted Ps is moving away from the sample surface $[p_\perp > 0]$, we can separate the Ps momentum distribution from the p-symmetric annihilations due to bulk and surface positrons in the Al by inversion and subtraction.[8,9,15]

Figure 1 contains 2D projections of the Ps spectra from three Al surfaces and some theoretical predictions. The fraction of the positrons forming Ps is indicated on each frame. The total number of counts in each Ps spectrum is $\approx 4 \times 10^4$. Because there should be theoretically no antisymmetric component, the data have been symmetrized about the $p_\perp$ axis to display the anisotropies better.[15] The data extend to a maximum radial momentum of ≈ 4.5 mrad, consistent with the measured value of $-\phi_{Ps}$.[7] We note that the Ps momentum distributions for Al(100) in Figs. 1(a) and 1(b) have three statistically significant lobes which are absent from the Al(111) data in Fig. 1(c). To determine whether the anisotropy is sensitive to azimuthal orientation, Fig. 1(b) shows the contours from Al(100) rotated by 45°. The slight

differences seen between Figs. 1(a) and 1(b) are not statistically significant. The experiment on Al(100) has been repeated several times on repolished and recleaned surfaces and the anisotropy is the same within statistics.

For comparison, we show in the bottom of Fig. 1 the contour lines corresponding to the predictions of the simplest theory for Ps emission.[7,10] The features of this Fermi "golden-rule" model are (a) an initial thermalized positron, (b) a nearly-free-electron conduction band, (c) a constant Ps-formation matrix element, and (d) conservation of $k_\parallel$ and energy. To obtain the surface-projected Al bands, we calculate the bulk band structure using Harrison's Al pseudopotential.[16] For each $k_\parallel$ in the surface Brillouin zone, $k_\perp$ is varied to generate the projected bands. The contours have been convoluted with a Gaussian corresponding to our measured detector resolution. The purely free-electron prediction shows a characteristic circular cutoff[8] corresponding to $-\phi_{Ps}$ but shows no anisotropy. An anisotropy resembling the characteristic lobes of the experimental spectra appears for Al(100) when we use the theoretical Al band structure [Fig. 1(d)]. In qualitative agreement with experiment, rotation by 45° causes only small changes [Fig. 1(e)]. The agreement between theory and experiment improves only slightly if we include a small contribution from surface-state electrons.[13] Near the surface where Ps forms, both bulk- and surface-state wave functions obtained from theory[14] are similar for Al; hence the anisotropy is mainly a density-of-states effect and stems from

the shape of the projected energy gaps around the center of the surface Brillouin zone. The energy gaps contribute much less to the anisotropy for Al(111) in agreement with Fig. 1(c); in fact, our theoretical prediction for Al(111) [Fig. 1(f)] is very similar to the free-electron prediction. Despite the reasonableness of the theoretical anisotropies, the experimental curves are not as peaked toward high momenta as the theory would suggest. The lower amplitude of the experiment relative to the theory at large $p_\parallel$ might indicate the presence of higher-order terms due to the emergence of the Ps nearly parallel to the surface. The increased amplitude of the experiment at small $|p|$ suggests that the matrix element for Ps formation might not be constant.[17,18]

With the use of several-hour counting times, we expect some effects due to contamination of the initially clean surfaces in Fig. 1. Figure 2 contains a sequence of Ps spectra from a separate run on Al(100) for which the vacuum conditions were not as good as in Fig. 1. The data in Figs. 2(a)–2(d) were taken at 3-h intervals following the initial preparation of the sample. We note that the anisotropy present in Fig. 2(a) gradually disappears and the momentum distribution narrows as we progress to Fig. 2(d). We attribute this effect to an increasing oxygen contamination. After the first 3-h run the contamination was roughly the same as it was initially, ≈ 0.006 ML C and ≈ 0.01 ML O as determined by a double-pass cylindrical-mirror Auger analyzer. After the fourth run [Fig. 2(d)] the C contamination was unchanged, but the O was found to have increased to 0.12 ML. The remarkable sensitivity to oxygen contamination could be an alternative reason for the enhanced low-momentum Ps relative to theory in Fig. 1, but further investigation of this effect is needed. A separate experiment shows that when a clean Al sample is exposed to 150 L (1 L $= 10^{-6}$ Torr sec) of oxygen, the Ps momentum distribution is indistinguishable from Fig. 2(d) and has the same Ps fraction.

The data of Figs. 1 and 2 confirm that the Ps formation is a surface-sensitive effect and that there is an anisotropy in the Ps momentum distribution that is a property of the clean Al(100) surface. It is clear that improved statistics and resolution are required before we can investigate different theories any further. On the other hand, we believe that the anisotropy of the data is established without a doubt, thus ruling out the possibility of large inelastic effects, and making it very likely that the Ps momentum spectra reflect the electron density of states near a metal surface. Given the recent introduction of an improved moderator[19] for obtaining a higher slow-positron intensity and the availability of better detectors, we should soon be able to examine the relative importance of surface states, d bands, umklapp effects, and the momentum dependence of the Ps-formation matrix element.

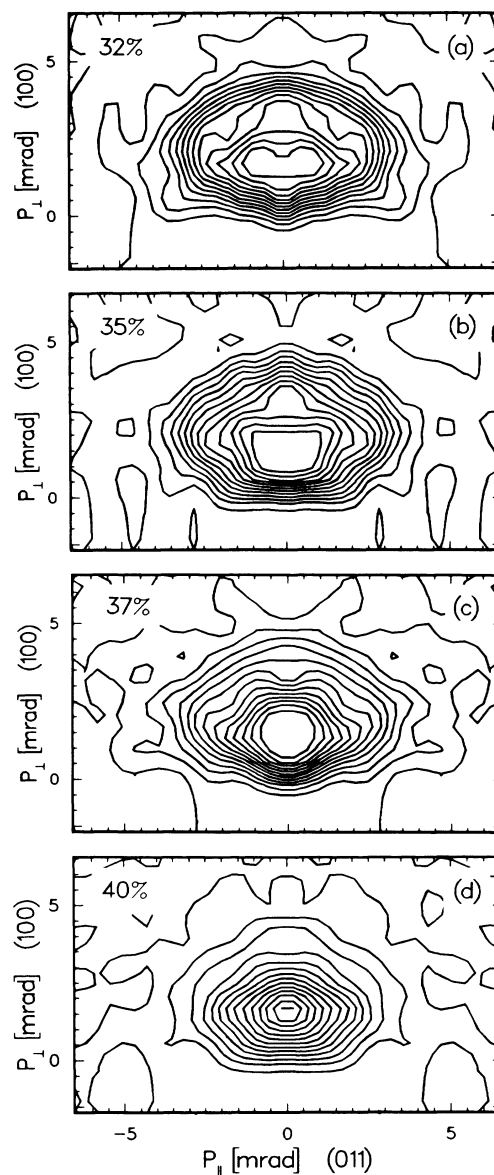The authors would like to thank E. M. Gullikson,

FIG. 2. 2D projections of the Ps-emission momentum spectra obtained at 3-h intervals with an initially clean Al(100) surface (a) showing a gradual change due to contamination by oxygen. Each spectrum contains $\approx 1.3 \times 10^4$ counts.

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[15]For perfect resolution, the $p_\perp < 0$ side is to be inverted through $\mathbf{p} = 0$ and subtracted from the $p_\perp > 0$ side. Because the finite detector resolution causes the Ps spectra to be smeared into the $p_\perp < 0$ region, we have deconvoluted the measured 2D-ACAR spectra before inversion and subtraction. To obtain the statistically most faithful result, the subtracted Ps spectra were convoluted with a 2D Gaussian representing the 1-mrad detector resolution. The precision of our data required us to find the momentum-space origin to within ± 0.05 mrad. For each run the $p_\perp = 0$ point was taken to be the center of a 2D-ACAR curve obtained with 15-keV positrons without altering the sample position. The residual Ps causes a shift of less than 0.05 mrad. The $p_\parallel = 0$ point was chosen to minimize the antisymmetric component of the data. Since the amplitude of this component was statistically consistent with zero, we have presented the symmetrized data in Figs. 1 and 2 to display the anisotropies more clearly.

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