**RAPID COMMUNICATIONS** 

PHYSICAL REVIEW B

## VOLUME 35, NUMBER 10

1 APRIL 1987

## Positronium time-of-flight spectroscopy of dissimilar metals

R. H. Howell, I. J. Rosenberg, and M. J. Fluss

Lawrence Livermore National Laboratory, University of California, Livermore, California 94550

R. E. Goldberg and R. B. Laughlin Department of Physics, Stanford University, Stanford, California 94305 (Received 24 October 1986)

Positronium velocity distributions using the time-of-flight technique have been determined for positronium emitted from clean, well-annealed, single-crystal samples of Al(111), Cu(100), Ni(100), and Au(100). The positronium energy distribution had a similar shape for all samples and was consistent with the hypothesis that positronium formation leaves behind a single electron hole in the conduction band of the metal. This was verified by explicit calculation for Ni, the first d-band metal to be studied by this technique.

It has long been recognized that positronium can be emitted from metallic samples bombarded by low-energy positrons.<sup>1</sup> Positronium emission is energetically favorable at the surface of many metals<sup>2</sup> and results from positrons that diffuse to the surface after slowing to thermal energies. The maximum energy available to positronium emitted from the surface is determined by the work functions of the positron and electron and the positronium binding energy. However, positronium leaves the surface of a material with a distribution of energies from zero to the work-function energy<sup>3,4</sup> that reflects the energy distribution of the bound electrons. A first-principles description of the electron-capture process does not yet exist. Mills, Pfeiffer, and Platzman,<sup>3</sup> suggested that positronium formation leaves behind a single electron hole in the conduction band of the metal, and the positronium spectrum may be calculated from the known dispersion relation of holes in the bulk by conserving momentum and energy at the electron-capture process. In this Rapid Communication, we test this idea by investigating the kinetic energy distribution of positronium emitted from several materials. We find that the spectra have a similar shape that is reasonably accounted for by the assumptions of Mills et al.,<sup>3</sup> although there are significant discrepancies at low energies for Au and Ni. We also find that the Ni spectrum is expected to have a shape similar to the simpler metals, despite the complexity of its band structure.

Positronium time-of-flight spectroscopy was performed with the pulsed, intense, variable-energy positron beam at the Lawrence Livermore National Laboratory 100-MeV electron linac. The beam was transported at 500 eV at a frequency of 1440 pulses per second, arriving at the sample with a pulse width of 15 ns. Positron energy at the sample was adjusted by a negative bias on the sample that also attracted all positrons that were emitted due to the negative positron work function. The intensity of the positron beam was limited to  $7 \times 10^4$  positrons per pulse to avoid spectral distortion due to detecting multiple events. The time-of-flight of positronium was measured between the beam arrival at the sample and the decay of a triplet positronium in front of the time-of-flight detector.<sup>5</sup> The time-of-flight detector was collimated by a slit 0.7 cm wide centered on a plane 10.5 cm in front of the sample. Positronium emitted at angles greater than either 15° or 30° was excluded by a variable aperture, circular collimator.

The measurements were performed in an ultrahigh vacuum chamber, base pressure  $1 \times 10^{-10}$  Torr, on the indicated simple surfaces of single-crystal samples of Al(111), Cu(100), Ni(100), and Au(100). Samples were sputter cleaned with Argon ions and annealed in a repetitive cycle until surface contamination, as observed by Auger analysis, was minimized, usually to below the limit of sensitivity of the analyzer. In the worst case, Ni, less than 10 at. % of carbon contaminated the surface.

The positronium time-of-flight spectra for all samples are shown in Fig. 1. These spectra contain both directly detected gamma rays from positronium decay and scattered gamma rays from positron decay outside the detector field of view. Thus, the peak at time zero results from the scattered decay gamma rays of either positrons that fail to escape the sample or singlet positronium. The width of the prompt peak defines the timing resolution and time was measured from zero at the peak centroid. The positronium time-of-flight data occurring at later times have been corrected for background and detector efficiency by the following procedure. A random background determined by the counts at very long time was first subtracted and then the data were corrected for the decay of triplet positronium by multiplying each channel by exp(t/142 ns). A second constant background due to scattered gamma rays from triplet positronium decay was then subtracted and the remaining spectrum was multiplied by a correction proportional to 1/t to correct for the variance in the time that positronium remained in the active region of the detector. Thus, the spectra displayed in Fig. 1 represent all triplet positronium from the sample emitted into the acceptance cone. The positronium energy distribution for the momentum component perpendicular to the sample surface can be obtained by multiplying the corrected time-of-flight counts by a factor proportional to  $t^3$ . In Fig. 2 are all of the spectra after transformation to the energy scale. The data at low energies, i.e., long time, have been summed into larger energy bins to enhance the statistics.

Positronium work-function values ( $\phi_{Ps}$ ) can be extracted from the time-of-flight spectra by extrapolating the front edge of the positronium peak to zero flux. The values of the work functions are Al,  $-2.78 \pm 0.28$  eV; Cu,  $-2.5 \pm 0.25$  eV; Ni,  $-2.63 \pm 0.26$  eV; and Au,  $-1.95 \pm 0.2$  eV, where errors from all factors are included. These values are in reasonable agreement with calculated values,<sup>6</sup> and are very close to those predicted by the measured values of the positron and electron work functions:



FIG. 1. Time-of-flight distributions of positronium emitted from clean metal samples. The data were background subtracted and corrected as described in the text. The peak at zero time results from the annihilations of singlet positronium and positrons remaining in the sample. The solid curves are distributions calculated from free-electron-energy distributions fitted to the work function and area under the curve.

Al, -2.60 eV; Cu, -2.45 eV; Ni, -2.58 eV; and Au, less than -1.7 eV.<sup>7</sup> This good agreement strongly supports the association of fast positronium with capture of a single electron from the Fermi surface.

The theory of Mills *et al.* proposes that the process of capturing an electron generates a single hole in the metal with a probability that is roughly independent of the hole's momentum. The distribution of positronium is then completely determined from conservation of energy and momentum in the plane of the surface  $\mathbf{k}_{\parallel}$  once the hole dispersion relation  $\varepsilon(\mathbf{k})$  is known. The component of momentum normal to the surface  $k_{\perp}$  is not conserved. A recombina-



FIG. 2. The data of Fig. 1 plotted as a function of the energy of positronium perpendicular to the sample surface.

5305

tion leaving behind a hole of momentum  $\mathbf{k} = (\mathbf{k}_{\parallel}, k_{\perp})$  produces a positronium with momentum  $\mathbf{k}_{\parallel}$  in the plane of the surface and a kinetic energy given by

$$\varepsilon_{\rm Ps} = -\phi_{\rm Ps} - \varepsilon_F + \varepsilon(\mathbf{k}) \quad , \tag{1}$$

where  $\varepsilon_F$  is the electron Fermi energy and  $\phi_{Ps}$  is the positronium work function.  $\phi_{Ps}$  is given in terms of  $\phi_+$  and  $\phi_-$ , the positron and electron work functions, and  $\varepsilon_b$ , the positronium binding energy, by

$$\phi_{\rm Ps} = \phi_+ + \phi_- - \varepsilon_b \ . \tag{2}$$

The component of positronium momentum q normal to the surface adjusts itself to satisfy energy conservation in the following manner:

$$\varepsilon_{\rm Ps} = \frac{\hbar^2}{4m} [|\mathbf{k}_{\parallel}|^2 + q^2] , \qquad (3)$$

where m denotes the electron mass. Since q is in practice less than  $k_{\perp}$ , energy conservation effectively "refracts" positronium away from normal emission, thereby depleting the spectrum of low-energy positronium. The number of

$$\frac{dN}{d\varepsilon_{\perp}} \simeq \frac{\alpha}{2(\varepsilon_F \varepsilon_{\perp})^{1/2}} \{ \varepsilon_{\perp} \tan^2(\gamma) \Theta[-\cos^2(\gamma)\phi_{Ps}' - \varepsilon_{\perp}] - (\phi_{Ps} + \varepsilon_{\perp}) \Theta[-\phi_{Ps} - \varepsilon_{\perp}] \Theta[\varepsilon_{\perp} + \cos^2(\gamma)\phi_{Ps}] \} ,$$
(5)

in the limit that  $\varepsilon_F \gg |\phi_{Ps}|$ .

The solid curves in Fig. 1 and Fig. 2 are plots of Eq. (5), multiplied by  $\sqrt{\varepsilon_{\perp}}$  and convoluted by a Gaussian resolution function with the parameters  $\alpha$  and  $\phi_{Ps}$  adjusted to fit the data. In all of the metals measured, the positronium distribution is matched by the model in the region from the maximum energy to positronium energy just below the peak energy. In Al and Cu the agreement is good at the lowest energies that are clearly resolved from the background of scattered positronium seen at long times (low positronium energies). The quality of this agreement is evidence that the assumption of Mills et al.<sup>3</sup> that a single hole remains is correct.

However, the ability of the free-electron theory to fit the nickel spectra is surprising because nickel is a *d*-band metal with a complicated band structure. The similarity of the nickel spectra to those of the simpler metals raises the possibility that the experiment is measuring not the hole dispersion, as Mills et al.<sup>3</sup> originally suggested, but some other property of the metal. To address this question, we have evaluated Eq. (4) using the band structure appropriate for nickel. For simplicity, we use a tight-binding fit to the self-consistent Korringer-Kohn-Rostoker calculations of Moruzzi, Janak, and Williams.<sup>10</sup> The tight-binding Hamiltonian assigns on-site and near-neighbor tunneling

TABLE I. Tight-binding matrix elements in eV for Ni, used to generate Fig. 3.

Es.	0.0	
Ed	0.0	
$V_{ss\sigma}$	-0.575	
V <sub>sdo</sub>	-0.591	
V <sub>ddo</sub>	-0.462	
V <sub>ddx</sub>	0.249	
V <sub>dd8</sub>	0.0	

positronium atoms emitted within an angle  $\gamma$  of normal and with a normal energy  $\varepsilon_{\perp} = (\hbar^2/4m)q^2$  between  $\varepsilon_{\perp}$ and  $\varepsilon_{\perp} + d\varepsilon_{\perp}$  is

$$\frac{dN}{d\varepsilon_{\perp}} = \frac{\alpha}{(\varepsilon_{\perp})^{1/2}} \int \Theta[\tan(\gamma) - |k_{\parallel}|/q] |\nabla_{\perp}\varepsilon(\mathbf{k})|^{-1} d\mathbf{k}_{\parallel} ,$$
(4)

where  $\Theta$  is 1, when its argument is positive, and zero otherwise and  $\alpha$  is a metal-dependent constant. In discussing the data we actually use a modified form of Eq. (4) from Pendry in which the factor  $\varepsilon_{\perp}^{-1/2}$  is absent. The difference between these two expressions results from the arbitrary choice of a constant matrix element<sup>3</sup> versus a constant probability for electron pickup.<sup>4,8</sup> The constant probability formation has been retained so that the present analysis will be consistent with our analysis of surface-angularcorrelation measurements of positronium performed on copper and lead.<sup>4,9</sup> If the dispersion relation is that of free electrons  $[\varepsilon(\mathbf{k}) = (\hbar^2/2m) |\mathbf{k}|^2]$ , then Eq. (4) may be integrated to yield

$$= \frac{\alpha}{2(\varepsilon_F \varepsilon_\perp)^{1/2}} \{ \varepsilon_\perp \tan^2(\gamma) \Theta[-\cos^2(\gamma)\phi_{Ps}' - \varepsilon_\perp] - (\phi_{Ps} + \varepsilon_\perp) \Theta[-\phi_{Ps} - \varepsilon_\perp] \Theta[\varepsilon_\perp + \cos^2(\gamma)\phi_{Ps}] \},$$
(5)



FIG. 3. Comparison of experimental positronium energy spectrum (boxes) with that predicted by Eq. (4) (dashed lines) using the tight-binding bond structure described in the text. The solid curve is the dashed curve smoothed in time domain by a Gaussian resolution function. The detector aperture is 15° (top) and 30° (bottom). The inset shows the energy bands from  $\Gamma$  to X.

matrix elements between the one s orbital and the five dorbitals assumed to reside on each nickel atom. The matrix elements, which we obtain from Harrison,<sup>11</sup> are listed in Table I. The band structure produced by this Hamiltonian is shown along the line  $\Gamma \rightarrow X$  in the inset of Fig. 3. The numerical evaluation of Eq. (4), both as originally calculated and as smoothed to account for the 30 ns detector resolution, is compared with the data in Fig. 3. As with Figs. 1 and 2, the parameters  $\phi_{Ps}$  and  $\alpha$  have been adjusted to fit the overall height and high-energy edge of the data. One sees that the gross features of the theory, that is the continuous growth of the signal as energy increases from zero, the peak, and the continuous diminution to zero at high energy, are the same as those of the free-electron theory, even though the band structure is very different from that of a free electron metal. This is because the fall-off at low energies is due to "refraction," while the fall-off at high energies is actually a sharp cutoff at the Fermi surface broadened by the detector's ability to measure only  $\varepsilon_{\perp}$ , as opposed to  $\varepsilon_{Ps}$ . The quantitative agreement between theory and experiment on the high-energy edge of the peak is significant, even though it is very sensitive to the detector resolution function. The fit of the solid

- <sup>1</sup>K. F. Canter, A. P. Mills, Jr., and S. Berko, Phys. Rev. Lett. 33, 7 (1974).
- <sup>2</sup>R. Nieminen and J. Oliva, Phys. Rev. B 22, 2226 (1980).
- <sup>3</sup>A. P. Mills, Jr., Loren Pfeiffer, and P. M. Platzman, Phys. Rev. Lett. 51, 1085 (1983).
- <sup>4</sup>R. H. Howell, P. Meyer, I. J. Rosenberg, and M. J. Fluss, Phys. Rev. Lett. **54**, 1698 (1985).
- <sup>5</sup>R. H. Howell, I. J. Rosenberg, and M. J. Fluss, Phys. Rev. B 34, 3069 (1986).
- <sup>6</sup>R. Nieminen, in *Positron Solid State Physics*, edited by W. Brandt and A. Dupasquier (North-Holland, Amsterdam, 1983).

curve in Fig. 2, which is broadened similarly, is visibly poorer. Theory and experiment do not agree well at low energies in either nickel or gold. The nickel data with  $\gamma = 15^{\circ}$  in Fig. 3 suggest that the very-low-energy divergence seen in the  $\gamma = 30^{\circ}$  data is due to a scatter of positronium, but that the excess signal near 1.0 eV is real and is a failure of the theory. The discrepancy in this region can be reduced marginally (20%) using the constant matrix element form of Eq. (5) rather than the constant pick-up probability version. We believe that the most likely cause of this discrepancy is a surface effect. It should be remarked that the theory results in a legitimate prediction that is not expected to be destroyed by including magnetism. The absence of the predicted structure in the data is a puzzle.

This work was supported in part by the National Science Foundation under Grant No. DMR 8510062. This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48 with special support from Institutional Research and Development funds.

- <sup>7</sup>A. P. Mills, Jr., in Ref. 6.
- <sup>8</sup>J. Pendry, in Ref. 6.
- <sup>9</sup>R. H. Howell, I. J. Rosenberg, P. Meyer, and M. J. Fluss, this issue, Phys. Rev. B 35, 4555 (1987).
- <sup>10</sup>V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978), p. 93.
- <sup>11</sup>W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980), Chap. 20.