Gamma Spectra Resulting from the Annihilation of Positrons with Electrons in a Single Core Level

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The first gamma spectra associated with the annihilation of positrons with individual core levels (Cu $3p$ and Ag $4p$) are presented. The spectra were obtained by measuring the energy of γ rays time coincident with Auger electrons emitted as a result of positrons annihilating with a selected core level. Relativistic calculations show good agreement with experiment over a limited range of momenta. However, statistically significant differences indicate that the measurements can provide an impetus to new calculations of many body effects in positron-core electrons annihilation.

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Positron annihilation spectroscopies are among the most sensitive probes of open volumes in condensed matter and of the momentum distribution of electrons in alloy systems [1–3]. The contribution to the gamma (γ) spectra from annihilation with core electrons has become a subject of interest as the result of recent experiments demonstrating that a chemically distinct core signature makes it possible to obtain element-specific information in positron defect studies [4–6]. Typically more than 90% of the annihilation events occur with the valence electrons due to the repulsion of positron from the positive core. Until now it has not been possible to experimentally separate the core-electron contribution from the much larger valence contribution to the annihilation spectra.

We report the first measurement of the Doppler-broadened γ-ray energy spectra associated with the annihilation of a positron with a selected, individual, core level. The measurement method relies on the fact that almost all of the annihilation events with the outer core electrons result in the almost simultaneous emission of an energetic electron resulting from a core-valence-valence (CVV) Auger transition in which one valence electron carries off the energy made available when another valence electron fills the core hole left by annihilation. Previous measurements have demonstrated that it is possible to detect these annihilation-induced Auger electrons with high efficiency and with an energy resolution sufficient to infer the energy level of the initial core hole [7,8]. Thus, γ spectra associated with positron annihilation with electrons in a particular core level can be obtained by measuring the energies of γs detected in coincidence with annihilation-induced Auger electrons of the appropriate energy.

The experimental measurements of the annihilation γ spectra of individual core levels provide a stringent test of theoretical calculations of core annihilation momentum distributions and a guide to the construction of improved descriptions of the electron-positron correlation effects as they pertain to annihilation with core electrons. The results reported here can be expected to impact on a broad range of surface and positron spectroscopies and provide information necessary in the proper interpretation of recent $\gamma - \gamma$ coincidence studies of the chemical environment of defects. In addition, the experimental method reported here provides a means of measurement of the effects of adsorbates and reduced coordination on the core-level momentum densities of atoms at the surface.

Positrons in solids annihilate predominantly into two γ rays that are equal in energy and antiparallel in the center of mass frame. In the laboratory frame, the center of mass motion of the positron-electron pair results in a Doppler shift of magnitude, $(P_L c)/2$, yielding energies, $E_{\gamma 1}$ and $E_{\gamma 2}$, for the two annihilation γ rays:

$$E_{\gamma 1} = m_0 c^2 - E_B/2 + (P_L c)/2 \quad \text{and} \\ E_{\gamma 2} = m_0 c^2 - E_B/2 - (P_L c)/2, \tag{1}$$

where m_0 is the rest mass of the electron (positron), c is the speed of light, E_B is the binding energy of the electron, and P_L is the component of the center of mass momentum of the electron-positron pair along the direction of the γ-ray emission. Consequently, the energy spectrum of annihilation γ's is proportional to a one-dimensional projection of the momentum distribution of electron-positron pairs at the time of annihilation given approximately by

$$\rho(\mathbf{p}) = \pi r_0^2 c \sum_i \left| \int d\mathbf{r} e^{i\mathbf{p}\cdot\mathbf{r}} \Psi_+(\mathbf{r}) \Psi_{-i}(\mathbf{r}) \sqrt{\Gamma_i(\mathbf{r})} \right|^2, \tag{2}$$

where r_0 is the classical electron radius, $\mathbf{p}$ is the total momentum of the annihilation pair, $\Psi_+(\mathbf{r})$ is the positron wave function, $\Psi_{-i}(\mathbf{r})$ is the wave function for the ith electron, and $\sqrt{\Gamma_i(\mathbf{p}, \mathbf{r})}$ is a weighting function that models enhancement, i.e., electron-positron correlation effects which lead to an annihilation rate higher than that predicted in the independent particle approximation [9].

Conventional measurements (including those using $\gamma - \gamma$ coincidence techniques [10]) probe the total momentum density of the system. In modeling these data, Eq. (2) must be summed over all occupied electron states. Thus conventional spectra must be compared with calculations of sums of individual level momentum densities weighted by momentum dependent enhancement factors that introduce uncertainties that seriously limit the reliability of the comparison.

Accurate calculations of the annihilation γ spectra needed to extract chemical information in positron defect studies will require the ability to model the enhancement factor, $\Gamma(\mathbf{p}, \mathbf{r})$, for core levels. Although adequate for the valence band, the local-density approximation (LDA) can be expected to break down for the core levels because of their wide range of momenta and large electron density gradients [11]. The γ spectra of individual core levels obtained using the γ-Auger technique provide a stringent test of theoretical efforts to go beyond the LDA such as the generalized gradient approximation [12] and explicitly nonlocal treatments [11] such as the weighted density approximation. It is important to note that γ-Auger coincidence permits the simultaneous measurement of both the low and high momentum parts of the annihilation spectra for a single core level that provides a test of attempts to model the momentum dependence of γ [13].

The γ-Auger coincidence data were acquired using a magnetically guided positron annihilation-induced Auger system [15] with the addition of a high purity Ge (HPGe) detector, multichannel analyzer (MCA), and fast coincidence circuitry (Fig. 1). The positron beam was incident on the high purity (99.999%) foil samples at 12 eV. The surfaces of the samples were periodically sputtered and annealed to maintain cleanliness. Conventional Auger surface analysis indicated that surface impurities (mostly C and O) remained below 5% during the period of data acquisition. Electrons emitted from the sample were guided through an energy analyzer and detected by means of a microchannel plate. The γ energies were measured using the HPGe detector, mounted perpendicular to the positron beam, 0.058 m from the sample, and behind a 0.0016 m stainless steel vacuum window. The full width at half maximum (FWHM) of the detector resolution function was measured to be 1.23 keV using a ^{85}Sr calibration source.

Annihilation γ-energy spectra were acquired in coincidence with the detection of annihilation-induced Auger electrons by gating the input of the MCA with a pulse resulting from the detection of electron in the selected energy range within 600 ns of the detection of the γ ray. The annihilation γ spectra of the $4p$ level of Ag was acquired by requiring coincidence with electrons in the energy range 35–38 eV corresponding to the peak of the energy distribution of the Auger transition resulting from the filling of a $4p$ hole. Similarly, spectra of the Cu $3p$ level was acquired by requiring coincidence with electrons in the range of 57–59 eV. "Noncoincidence" (core + valence) γ spectra were obtained by setting the gate input high, thus allowing all of the HPGe pulses into the MCA.

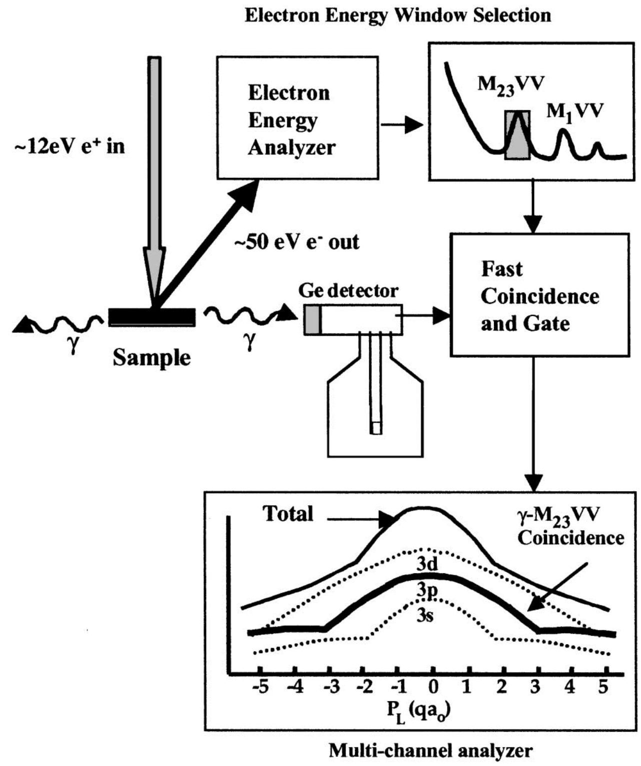

FIG. 1. Schematic diagram of the γ-Auger coincidence measurement system. A low energy positron beam is used to place positrons at the sample surface. The γ energy was measured using a HPGe detector connected to a multichannel analyzer (MCA). The Auger electrons were energy selected using an $\mathbf{E} \times \mathbf{B}$ filter and detected using a microchannel plate. The Doppler-broadened γ spectrum for a selected core level was acquired by opening a gate to the MCA only after the simultaneous detection of a γ ray and an electron from an Auger transition resulting from the annihilation of the selected level. Conventional Doppler-broadened spectra were acquired by holding the MCA gate open.

The kinetic energy of the positrons hitting the surface ($\sim$ 12 eV) was below the core-electron impact-ionization threshold ensuring that the Auger electrons detected resulted from core-electron annihilation [7]. Note that a large fraction of the positrons injected into the samples at 12 eV diffuse back to the surface and become trapped in an image-correlation well before they annihilate. This greatly increases the escape probability of the Auger electrons and implies that the γ-Auger coincidence technique predominantly samples atoms in the topmost atomic layer.

A small background ($\sim 5\%$ of the total intensity for Cu and 11% for Ag) due to accidental coincidences between the γ signal and uncorrelated microchannel plate pulses was determined directly from a measurement of the integrated intensity of the γ signal taken in coincidence with electrons detected in an energy range where no true coincidences are present (20 eV above the annihilation-induced Auger peak). The accidental contribution was then removed by subtracting high statistics, noncoincidence

γ spectra scaled according to the measured intensity of the accidental contribution to the spectra. We note that the γ-Auger coincidence, like the $\gamma - \gamma$ coincidence, eliminates background due to Ps, nuclear decay and cosmic ray γs ,etc. However, only γ-Auger coincidence is capable of separating the core part of the annihilation spectra from the much larger (20 times at the peak) valence contribution.

Figure 2 shows a comparison of the energy distribution of annihilation γ rays from Cu [Fig. 2(a)] and Ag [Fig. 2(b)] measured in coincidence, and without coincidence with an Auger electron emitted as a result of filling the $3p$ core hole in Cu and the $4p$ core hole in Ag, respectively. The curves were scaled to have the same maximum. For Cu, the FWHM of the noncoincidence spectra is 2.2 keV, consistent with the fact that this spectrum is dominated by the narrow valence contribution. In contrast, the γ spectra taken in coincidence with the Auger electron is more than twice as wide (FWHM = 4.7 keV), reflecting the fact that only contributions from the broad momentum distribution associated with the highly confined radial wave functions of the core level remain. We note that there is a small low energy tail on both spectra due to incomplete charge collection in the Ge detector. The coincidence spectrum corresponding to annihilation with the $4p$ level of Ag was found to be ~12% narrower than the spectrum resulting from annihilations with the $3p$ level of Cu. This difference can be understood qualitatively in terms of the differences in binding energies of the two levels (60 eV for the Ag $4p$ vs 76 eV for the Cu $3p$). The fact that the Ag $4p$ is less tightly bound than the Cu $3p$ implies that the Ag level is wider in real space and hence narrower in momentum space.

Figure 3 shows a comparison between an LDA-based theoretical calculation and the one-dimensional momentum distribution of the electron-positron pairs obtained by transforming the abscissa of the coincidence spectra from γ energy to electron-positron pair momentum using Eq. (1). The momentum is expressed in dimensionless atomic units, where q is the wave vector and a_0 is the Bohr radius. The Cu $3p$ curve has a shoulder starting at $4.5qa_0$, while the Ag $4p$ curve has a shoulder at $3.8qa_0$. The calculations were based on an atomic code using a local-density form for the electron-positron correlation function [14], with no explicit momentum- or density-dependent enhancement. The calculations include appropriate integration of the 3D radial momentum distribution to correspond to the 1D Doppler measurements. As a result of the integration, nodes in the radial momentum distributions result in breaks in momentum that appear as shoulders in the 1D momentum distribution.

Overall, the agreement between the theory and experiment is remarkable given the complexities of both the experiment and theory and the fact that the calculations were done independently with no adjustable parameters aside from the overall normalization. However, referring to Fig. 3 it may be seen that there are differences with theory that are well outside of the statistical uncertainties of the

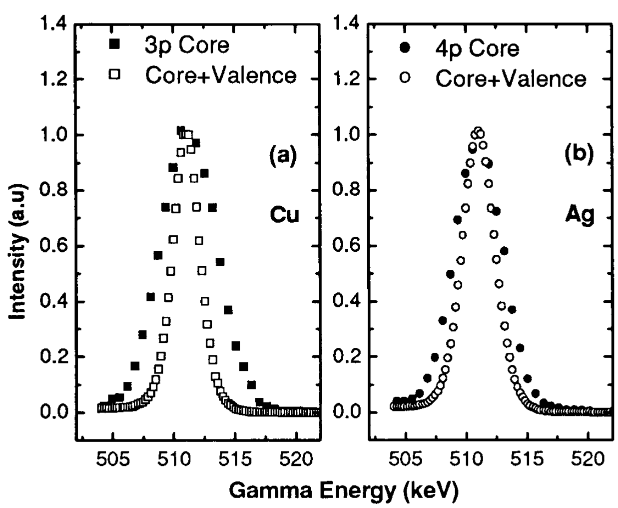

FIG. 2. Comparison of the "core + valence" and "core" annihilation γ-ray energy spectra resulting from the bombardment of polycrystalline Cu (a) and Ag (b) foils with a 12 eV positron beam. The core + valence spectra (open symbols) were acquired without a coincidence requirement. The core spectra (solid symbols) were acquired in time coincidence with the detection of an electron in the range of the peaks of the energy distribution of Auger electrons emitted as a result of the annihilation of a positron with the Cu $3p$ (M_{23}) and Ag $4p$ (N_{23}) electrons for (a) and (b), respectively.

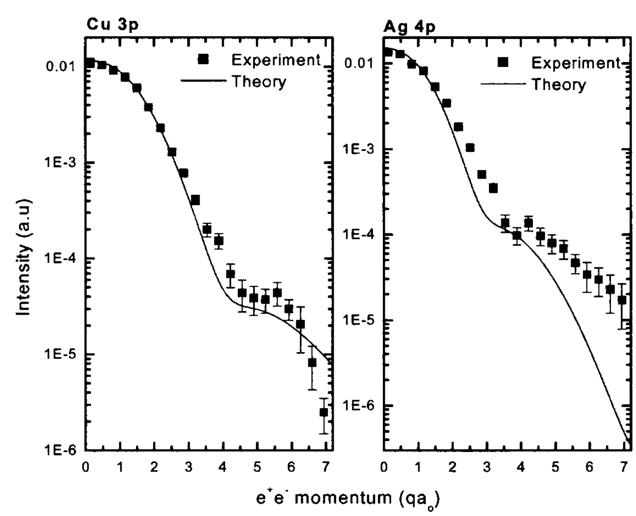

FIG. 3. Momentum distribution of positron-electron pairs for the Cu $3p$ and the Ag $4p$ core states. The experimental distributions (solid squares) were extracted from Doppler-broadened γ spectra (shown in Fig. 2(b) for Cu) by using Eq. (2) to convert the annihilation γ energy to electron-positron pair momentum (given in dimensionless units, qa_0, where q is the wave vector and a_0 is the Bohr radius). The measured distributions (solid squares) are compared to theoretical calculations (see text) shown as solid lines.

experiment. Specifically, when both theory and experiment are area normalized, the calculation for Cu lies consistently below the experimental values from a qa_0 of ~3 to ~6, while for Ag there is a shift of about 1 unit in the position of the shoulder at $qa_0 - 3.8$ and the calculations fall well below the experiment for values of qa_0 above ~4. This indicates that the calculations are not predicting the correct ratio of high momentum to low momentum spectral weight. We note that our measurements are the first to directly separate the low momentum contributions of the core from the much larger signal from annihilation with valence electrons.

There are a number of possible explanations for the discrepancies between theory and experiment: (1) The LDA-based calculation of the core-electron momentum distribution may underestimate the high momentum tails. However, while the LDA is known to give the wrong core-level binding energies, the charge densities from which the momentum distributions are calculated are believed to be accurate. (2) The discrepancies may be due to the level of approximation used in modeling the positron wave function in which only an s-like state was included. While s states have appeared to be adequate for approximating the positron state in bulk calculations, it is likely that a mixed s-p state may be more appropriate for the overlap of a positron in a surface state with a surface atom. We note, however, that the observed discrepancies appear to be in the high momentum region in which the positron s contribution to the total pair momentum could be expected to be small due to the fact that, on the average, the positrons are at thermal energies at the time of annihilation. (3) The discrepancy may reflect inadequacies in the treatment of electron-positron correlation effects and the need for an enhancement term with an explicit momentum dependence that increases at higher momentum. We note, however, that current treatments of the momentum dependence of the LDA-based theories predict the opposite momentum dependence.

The method of using coincidence with the detection of Auger electrons to select core annihilation events, while used in this study to measure the Doppler-broadened γ spectra, is of general applicability in studies of core annihilation. Future γ-Auger coincidence measurements could be used to measure the core spectra of impurity atoms at the surface. The core signatures of impurities thus obtained could then be used to provide confirmation of the signatures of vacancy-impurity complexes in the bulk as seen in Doppler spectra obtained using $\gamma - \gamma$ coincidence [4]. The Auger coincidence technique can also be used in conjunction with the measurement of the angular correlation of annihilation radiation (ACAR) in high-resolution fundamental studies of core-electron momentum distributions.

The first measurements of the Doppler-broadened γ spectra resulting from the annihilation of positrons with individual core levels have been presented. Annihilation γ spectra from the $3p$ core level of Cu and the $4p$ core level of Ag were obtained by measuring the energies of γ rays time coincident with Auger electrons emitted as a result of positrons annihilating with the selected core level. A comparison with calculations of the annihilation spectra for these core levels shows excellent qualitative agreement. However, statistically significant discrepancies between theory and experiment at high momentum suggest the need to improve the treatment of many body electron-positron correlation effects in annihilation as they pertain to core levels. Future applications of the γ-Auger coincidence technique include identification of impurity-induced changes in core spectra obtained from the surface and studies of core-electron momentum densities.

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