

Giant Coster-Kronig Transitions and Intrinsic Line Shapes of the Anomalous Pd $M_{45}VV$ Auger Spectrum of Pd/Ag(100) Dilute Surface Alloys

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The Pd M_4VV and M_5VV Auger spectra of the 0.1 ML Pd/Ag(100) dilute surface alloy have been measured using Auger-photoelectron coincidence spectroscopy. The M_4VV spectrum indicates that Pd $3d_{3/2}$ core holes have a Coster-Kronig decay rate that is ~ 10 times that of Pd metal. Our calculations show that this giant enhancement arises from the local electronic structure of excited Pd atoms at the surface. Anomalous features in the Auger line shape are similar to those seen in dilute bulk PdAg alloys, and these features in the M_5VV and M_4VV lines are in good agreement with theoretical predictions.

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Dilute transition metal alloys have garnered both scientific and technological interest for many years. These systems often exhibit unusual magnetic, transport, or optical properties that are quite distinct from those of their constituents [1,2]. Surface alloys are particularly interesting as they offer the possibility of reduced cost while retaining the desirable aspects of the alloy. The interesting properties of these systems typically are governed by the relative binding energy of the d electrons in the two parent materials. An excellent example is $\text{Pd}_x\text{Ag}_{1-x}$ ($x \sim 0.1$), which is regarded as a realization of the Anderson impurity model [3]. Photoemission studies of this system provided direct evidence that the Pd d levels interact with the Ag sp continuum to form a virtual bound state [4–6]. Similarly, the Pd $M_{45}VV$ Auger spectrum from dilute $\text{Pd}_x\text{Ag}_{1-x}$ ($x \sim 0.1$) alloys [7–16], and to a lesser extent $\text{Pd}_x\text{Cu}_{1-x}$ [8,17,18], has an anomalous line shape that contains features with no counterparts in the Pd metal [19–22]. The origin of these features has been controversial for many years with respect to the nature of the interaction of the Pd d levels with the Ag sp and d levels [7,10,11]. Explanations for the line shape range from a local Pd density of states (DOS) that is dominated by a virtual bound state [12,16] to the existence of two stable two-hole states bound to the Ag site [13–15]. Both theories are in close agreement with each other regarding the shapes of the anomalous components in the M_4VV and M_5VV transitions, but these lines have never been isolated nor the line shapes verified.

Core hole excitation and decay processes are receiving increased attention as a means of probing charge transfer on femtosecond time scales [23]. In addition, Coster-Kronig (CK) transitions are of particular interest because they may provide an effective way to rapidly depopulate intermediate states and thereby facilitate establishing the population inversions needed for x-ray lasing [24]. The behavior of the Pd M_4M_5 CK transition, where the $3d_{3/2}$ core hole is filled by a $3d_{5/2}$ electron (generating an accompanying electron-hole pair excitation), has been extensively studied [22,25,26]. As Pd is the last member of the $4d$ transition metal group, small changes in the local Pd valence levels may have a large impact on the probability of CK transitions.

In this Letter, we report the results of an Auger-photoelectron coincidence spectroscopy study of the dilute Pd/Ag(100) surface alloy [27,28]. We find that this surface alloy exhibits an anomalous $M_{45}VV$ line shape similar to the dilute bulk alloy [7–16] and that the anomalous features in the M_5VV spectrum and in the high kinetic energy (KE) part of the M_4VV spectrum are well described by theoretical calculations [12–16]. However, the coincidence M_4VV spectrum also contains about an order of magnitude more spectral weight at low KE than is found for Pd metal. This emission indicates a strongly enhanced probability for Coster-Kronig decay of Pd $3d_{3/2}$ core holes in the surface alloy. First principles calculations show that this channel is significantly enhanced owing to modifications of the local Pd DOS

in the surface alloy system in the presence of the $3d$ core hole.

All of the data reported here were acquired at beam line U16B of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Synchrotron radiation from the vacuum ultraviolet storage ring is dispersed by a monochromator and focused to a small spot on the sample. The spectrometer, which is described in detail elsewhere [29,30], has two cylindrical mirror analyzers (CMAs) that are aligned to the illuminated spot. To obtain coincidence Auger (photoemission) spectra, one CMA remained at a fixed kinetic energy corresponding to the peak of the core photoelectron (Auger electron) spectrum while the second CMA scanned kinetic energy through the associated Auger electron (photoelectron) spectrum. Electrons that are detected in the two CMAs within 20 ns of each other are accepted as valid coincidence events. This signal includes both true (originating from the same excitation) and accidental (originating from fortuitously “simultaneous” excitations at different sites) counts. To determine the accidental rate, a second delayed coincidence spectrum is also measured. The true coincidence spectra presented here are obtained by subtracting the accidental spectra from the total coincidence spectra. For comparison purposes, a conventional, noncoincidence (also called singles) photoemission spectrum is acquired along with the coincidence data. For all of the measurements reported here, the photon energy was 470 eV and the energy resolution was 0.72 eV (photons + electrons).

The dilute Pd surface alloy was prepared by *in situ* vapor deposition of 0.1 monolayer of Pd onto a Ag(100) crystal. The Ag single crystal surface was known to produce sharp LEED and Laue x-ray diffraction patterns. Prior to deposition of the Pd, the Ag(100) surface was cleaned by repeated cycles of sputtering (500 eV Ar^+ ions) and annealing (740 K for 15 min). Sample cleanliness was monitored *in situ* with soft x-ray photoemission spectroscopy, and cleaning cycles were repeated until no contamination could be detected. The Pd was deposited and coincidence data were acquired after the sample had returned to room temperature.

To investigate theoretically the relative Pd Coster-Kronig rates in bulk Pd and in the dilute Pd-Ag surface alloy, self-consistent full-potential augmented plane wave calculations [31,32] including the effect of a Pd core hole (Pd^*) were performed. We examined Pd^* in bulk Pd and in Ag (modeled by 32 atom supercells) and Pd^* in a $c(2 \times 2)$ arrangement at the (001) surfaces of Pd and Ag modeled by nine layer films. The structures were relaxed. Based on comparisons of the local density of states at sites away from the Pd^* site for calculations with and without the core hole, these systems are large enough that the direct core hole interactions on different sites will not affect the results here.

Figure 1(a) shows the singles $\text{Pd } M_{45}VV$ Auger spectra obtained from a thick Pd film and from the 0.1 ML

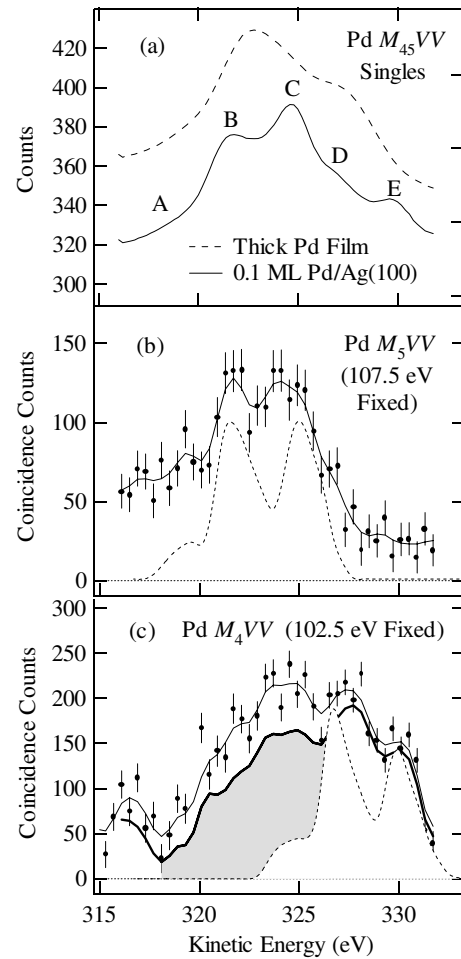


FIG. 1. (a) Photon excited singles $\text{Pd } M_{45}VV$ Auger spectra from bulk metallic Pd (dashed curve) and the dilute Pd/Ag(100) surface alloy. (b) $\text{Pd } M_{5}VV$ Auger spectrum obtained in coincidence with photoelectrons emitted at 107.5 eV (the nominal kinetic energy of the Pd $3d_{5/2}$ photoelectrons). (c) $\text{Pd } M_{4}VV$ Auger spectrum obtained in coincidence with photoelectrons emitted at 102.5 eV (the nominal kinetic energy of the Pd $3d_{3/2}$ photoelectrons). In panels (b) and (c), the data points with error bars are the coincidence data, the thin solid curve is a smooth fit to that data, and the dotted curve is a theoretical prediction for the $M_{5}VV$ and $M_{4}VV$ line shapes, respectively. In panel (c) the thick solid curve is the intrinsic $M_{4}VV$ line shape and the shaded region is an estimate of the Coster-Kronig contribution.

Pd/Ag(100) surface alloy. The spectrum from the surface alloy exhibits anomalous features labeled A through E that are similar to the bulk analog [7,22]. Feature C, which has no counterpart in the elemental spectrum, dominates the line. Moreover, as peak C lies midway between the two main features of the elemental Pd spectrum, it is unclear whether it is associated with the decay of $3d_{5/2}$ or $3d_{3/2}$ core holes. Figures 1(b) and 1(c) show the $M_{5}VV$ and $M_{4}VV$ Auger spectra obtained in coincidence with Pd $3d_{5/2}$ and $3d_{3/2}$ core level photoelectrons, respectively. The coincidence $M_{5}VV$ spectrum indicates that features A, B, and C of the singles spectrum are

associated with the M_5VV Auger transition. Furthermore, the line shape is well described by the theories of Vos *et al.* [12,16] and Hedegard *et al.* [13–15].

The M_4VV transition, on the other hand, is quite different. As seen in Fig. 1(c), the high KE structure, above ~ 326 eV, clearly indicates that features D and E are associated with the M_4VV transition [13–15]. These high KE features are also well accounted for by existing theory [12–16]. Much more pronounced, however, is the large amount of spectral weight in Fig. 1(c) at kinetic energies below 325 eV that is not anticipated in the calculations [13–15]. Figure 2 shows the Pd photoelectron spectrum from the surface alloy in the region of the $3d$ core levels. While most of the emission at 102.5 eV [the coincidence energy of the spectrum in Fig. 1(c)] is from primary Pd $3d_{3/2}$ photoelectrons, a portion is from inelastically scattered Pd $3d_{5/2}$ photoelectrons and can contribute to the as-acquired coincidence spectrum [22,33,34].

Also shown in Fig. 2 is the Pd $3d$ spectrum obtained in coincidence with Auger electrons emitted at 321.7 eV (i.e., the kinetic energy of feature B in the Auger spectrum). The thick solid curve is the result of a fit to the coincidence spectrum where a Gaussian plus an integrated background model each core level [22,33,34]. The fit shows that $2/3$ of the coincidence events at 102.5 eV are associated with $3d_{3/2}$ core holes and $1/3$ with $3d_{5/2}$ core holes. Therefore, $1/3$ of the intensity at 321.7 eV in the coincidence spectrum of Fig. 1(c) is attributable to Pd M_5VV Auger transitions. Accounting for this gives the thick solid curve in Fig. 1(c). The remaining difference between this curve and the theoretical line shape [i.e., the shaded region in Fig. 1(c)] is attributed to the M_4M_5 CK transition followed by an M_5VV decay. The spectral

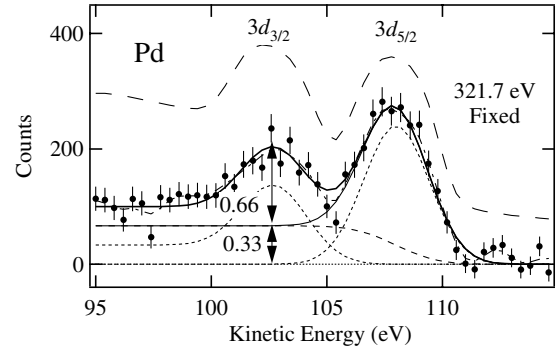


FIG. 2. The singles (long-dashed curve) and coincidence (data points with error bars) Pd $3d$ core level spectra from the dilute Pd surface alloy. The thick solid curve is a fit from which one can determine the fractional contribution of Pd $3d_{3/2}$ and Pd $3d_{5/2}$ photoelectrons to the emission at a kinetic energy of 102.5 eV.

weights of the direct and CK channels are comparable and thus their relative probabilities are approximately equal. In comparison, in elemental metallic Pd the direct Auger decay of $3d_{3/2}$ core holes is about ten more likely than the CK transition [22,25].

The dramatic increase in the CK transition rate can be understood by considering local density of states (LDOS) for Pd in the presence of a $3d$ core hole (denoted Pd*). Figure 3 shows such calculations for several different structures. The DOS all have low weight and are rather featureless above the d -band cutoff (which is at ~ -2.5 eV for the Ag hosts and $\sim +0.25$ eV for Pd). There is also a large relative increase in the unoccupied LDOS at the surface compared to the bulk. The calculated probability of a Coster-Kronig transition between two core levels f_i and f_j separated in energy by Δ is given by

$$P \sim \sum_{kk'} |\langle \phi_j(1)\psi_k(2) | r_{12}^{-1} | \Phi_{k'}(1)\phi_i(2) \rangle - \langle \phi_j(1)\psi_k(2) | r_{12}^{-1} | \Phi_{k'}(2)\phi_i(1) \rangle|^2 \delta(\Delta + \varepsilon_k - \varepsilon_{k'}),$$

where ψ_k and $\Phi_{k'}$ are occupied and unoccupied valence states, respectively. For the $3d_{3/2} \rightarrow 3d_{5/2}$ CK transition, the lowest order $l = 0$ term in the expansion of $|r_{12}^{-1}| = |r_1 - r_2|^{-1}$ will have a contribution from only the direct (first term above) process, which is localized on the site. At this level, the CK rate can be described approximately in terms of an (energy-dependent) matrix element and a joint density of states of the d states at the site:

$$P \sim \int_{E_F - \Delta}^{E_F} d\varepsilon |M(\varepsilon, \Delta)|^2 n(\varepsilon)n(\varepsilon + \Delta).$$

The calculated CK transition probabilities as a function of Δ for Pd* in these four structures are shown in the inset in Fig. 3. For $\Delta \approx 5$ eV (the experimental Pd $3d_{3/2} - 3d_{5/2}$ splitting), there is approximately a factor of 3 increase for the surface alloy compared to bulk Pd. This sizable increase is also seen for the Pd surface, but, as the Pd M_5VV transition has a substantial bandlike contribution

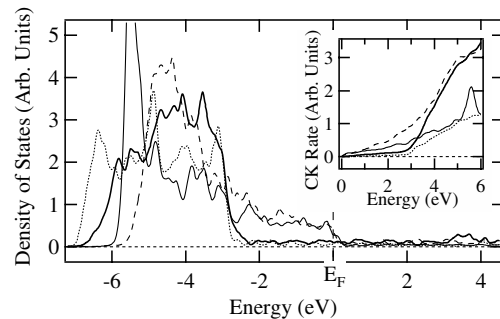


FIG. 3. Calculated Pd local density of states in the presence of a $3d$ core hole for a Pd atom in Pd bulk (thin solid curve), at the Pd(100) surface (dashed curve), in bulk Ag (dotted curve), and in a $c(2 \times 2)$ Pd/Ag(100) surface alloy (thick solid curve). Inset: CK transition probabilities for these systems as a function of Δ , the energy separation of the core levels.

in the energy range of the M_4VV line, such enhancement is difficult to observe experimentally. In singles measurements of the bulk Pd/Ag alloy, $\sim 1/3$ of the spectrum of this Auger line comes from the surface, which results in an apparent $M_4VV:M_5VV$ ratio that is smaller than anticipated from statistical and cross-section arguments. The enhanced rate is found to come mainly from the increase in the unoccupied DOS at the surface compared to the bulk; the integrated DOS from $E_F - \Delta$ to E_F are similar. Taking into account the Coulomb interaction of the Pd* d electrons [35] is expected to increase the CK rate by additional factors of 2–3, indicating that changes in local electronic structure should also contribute to the increased CK rate found for bulk alloys [7,11].

The manipulation of CK transition probabilities through modification of the LDOS, particularly through surface alloy formation, can have important implications. For example, it can provide a new way to vary the “core hole clock” when core level excitation and decay processes are used to study charge transfer on femtosecond time scales [23]. Moreover, a primary difficulty in obtaining appropriate conditions for x-ray lasing using core level transitions is producing the rapid depletion of the lower level so as to sustain a population inversion [24]. A promising approach to increase this rate is to deplete the lower level with a very fast CK transition. Our results suggest that it is possible to dramatically enhance the probability of CK transitions by appropriate manipulation of the local density of states through surface alloy formation.

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