Pd $M_{45}VV$ Auger spectrum determined by Auger-photoelectron coincidence spectroscopy: Intrinsic line shape and Coster-Kronig transitions

M. T. Butterfield* and R. A. Bartynski†
Department of Physics and Astronomy, Rutgers University, 136 Frelinghuysen Road, New Brunswick, New Jersey 08855

S. L. Hulbert
National Synchrotron Light Source, New York Brookhaven National Laboratory, Upton, New York 11973
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We have performed an Auger-photoelectron coincidence spectroscopy (APECS) study of the Pd $M_{45}VV$ Auger transition to ascertain the intrinsic line shapes of the M_4VV and M_5VV transitions at high-energy resolution (0.72 eV considering electrons and photons). The line shapes cannot be described by a simple self-convolution of the valence-band density of states, but are well described by the Cini-Sawatzky (CS) theory when it is applied separately to each component of the multiplet structure of the d^8 Auger final state. A fit to the APECS data using the sum of a CS distortion of the final-state multiplet splittings for the M_4VV and M_5VV Auger transitions indicates that the correlation energy of the most intense $^1G_4$ multiplet is 3.2 ± 0.1 eV. In addition, we find evidence that $(12\pm3)\%$ of the intrinsic M_4VV intensity is associated with Coster-Kronig-preceded Auger decays of $3d_{3/2}$ core holes.

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I. INTRODUCTION

The line shape of core-valence-valence (CVV) Auger spectra in transition metals has been the subject of numerous theoretical and experimental studies for many years.[1–13] Auger line shapes can be used to probe electron correlations in the valence band by comparing the measured Auger profiles against the prediction of various theories.[1,2,5,14–16] A common difficulty, however, is that Auger spectra associated with different core levels are often closely spaced in energy and cannot be resolved by conventional means. The technique of Auger-photoelectron coincidence spectroscopy (APECS) allows overlapping Auger spectra with different origins, e.g., due to different core holes, or containing multiplet or many-electron structure, to be distinguished. APEC spectra also exhibit a substantial reduction of the extrinsic inelastic secondary electron background. It is therefore an ideal experimental tool with which to investigate the local density of states in complex solids, such as dilute alloys and transition-metal compounds.[7–9,12,17–23] With APECS one can measure individual Auger line shapes and elucidate the components of which they consist.

If the on-site Coulomb energy U in the valence band of the system under study is small compared to the band width W, then the CVV Auger line shape is well described by a self-convolution of the density of states (SCDOS).[1,2] In contrast, if U is large then the spectrum becomes atomiclike and reflects the multiplet structure of the two-hole final states.[3] Cini and Sawatzky[5,14,15] (CS) independently developed a many-body model of Auger transitions that describes the continuous transformation of spectral weight on the Auger line shape between these two extremes for a closed band system. Similar to Ag, Pd is an interesting system because $U/W<1$, but not negligible, so it falls in this intermediate regime. Moreover, although Pd is technically an open-shell system, in the solid form it is missing only a fraction of an electron per atom (effectively a d^{9+} configuration). Therefore, Pd should provide an interesting test of whether the CS theory will also provide an accurate description of marginally open-shell systems.

There have been a number of experimental and theoretical studies of the Pd $M_{45}VV$ Auger transition. This is in part owing to the interest in dilute alloys of Pd in other $4d$ or $3d$ metals.[7–9,11,12,19,24–26] Vapor phase studies were carried out by Aksela, Harkoma, and Aksela,[27] who investigated the atomic Pd $M_{45}VV$ Auger line shape by means of electron-beam excitation and then compared the experimental results with theoretical profiles. A model profile based on the energies and intensities of the final-state d^8 multiplets, calculated in the nonrelativistic mixed coupling scheme, achieved good agreement with the experimental spectrum. Studies of the $M_{45}VV$ Auger line shape in dilute Pd alloys have previously been carried out by several groups to investigate impurity induced changes in the electronic structure of metals.[7–9,11,12,19,24–26,28] In certain alloys with a small Pd content, work has focused on the possibility that more than one type of localized two-hole state may be pinned to the impurity (i.e., Pd). Weightman and co-workers[7,9,11,12,19] experimentally investigated the Pd $M_{45}VV$ Auger line shapes in Pd_xCu_{1-x} and Pd_xAg_{1-x} alloys ($x\lesssim0.1$), and sought to explain the spectra in terms of the multiplet splitting of the Pd d^8 final state. For these alloys, they achieved a best fit to the data with a M_5VV:M_4VV intensity ratio of 1.0:0.3 using a value of 3.0 eV for the onsite Coulomb interaction of the $^1G_4$ multiplet. This is in contrast to a ratio of 1.0:0.69 predicted by calculations for pure Pd using the statistical occupancy of the core levels and their photoelectron cross sections. The experimentally determined reduction of M_4VV intensity was taken as evidence for a Coster-Kronig (CK) decay of $3d_{3/2}$ core holes. More precisely, a CK-preceded decay of the $3d_{3/2}$ level involves a $3d_{3/2}$ core hole being filled by a $3d_{5/2}$ electron accompanied by the excitation of an

electron-hole pair. The remaining $3d_{5/2}$ hole subsequently decays by an M_5VV transition in the presence of the additional valence-band hole. Thus, the CK transition would steal intensity from the direct M_4VV Auger decay. Moreover, the CK transition would result in the generation of a $3d_{3/2}$ photoelectron *and* an M_5VV Auger electron (perhaps shifted slightly in energy by the presence of the additional hole) that could be detected in coincidence.

To investigate further the nature of this CK transition, Creagh and Thurgate[29] carried out a low-resolution APECS study of the Pd $M_{45}VV$ Auger line shape. Considerable excess emission was observed when the M_4VV line was measured in coincidence with photoelectrons at the kinetic energy of Pd $3d_{3/2}$ photoelectrons. Attributing this emission to the CK transition yielded a M_5VV:direct-M_4VV intensity ratio of 1.0:0.3. In addition, a CK direct-Auger transition ratio for $3d_{3/2}$ core hole decay of 1.45:1.0, a value that is much larger than expected from core-level linewidths,[30] was determined. The first of these two ratios is close to the upper limit of the estimates by Weightman based on conventional Auger spectra from dilute Pd alloys. In Weightman's estimate, however, the CK contribution would be included in the M_5VV intensity, since it occurs at almost the same energy. Therefore, Creagh and Thurgate's estimate of the intensity in the M_5VV region to that in the M_4VV region is closer to 1.0:0.21, a value considerably larger than Weightman's result.

On the theoretical side, Cini and Verdozzi[16] carried out a study of the Pd $M_{45}VV$ line shape in an attempt to further extend the existing theory to open-shell systems and to include spin-orbit interactions, which had been neglected in previous treatments. The theoretical framework was then applied to Pd using both a matrix-type formulation and a weighted average of the spin projected $j=\frac{3}{2}$ and $j=\frac{5}{2}$ contributions to the local valence density of states. Both frameworks provided good agreement with the experimental Pd $M_{45}VV$ line shape although, as only conventional Auger spectra were available, they could not compare with the intrinsic line shapes.

In this paper, we report on a high-resolution APECS study of the Pd M_4VV and M_5VV Auger line shapes. These two Auger lines span an energy range of over 20 eV while their related core levels are separated by only about 5.5 eV. Thus these lines exhibit significant overlap and APECS provides an ideal tool to independently measure the two spectra. We have obtained M_4VV and M_5VV Auger spectra in coincidence with the emission from the $3d_{3/2}$ and the $3d_{5/2}$ core levels, respectively. An APECS measurement of the M_5VV Auger line directly reveals the intrinsic line shape of the transition. To ascertain the intrinsic M_4VV line shape, however, one must correctly account for inelastically scattered $3d_{5/2}$ photoelectrons that emerge at the same energy as primary $3d_{3/2}$ photoelectrons.[31,32] We find that the line shapes are well described if the CS theory is applied individually to each term of the Pd $4d^8$ multiplet with $U=3.2\pm0.1$ eV for the $^1G_4$ term. For both the M_5VV and the M_4VV Auger lines we observe emission most likely associated with a discrete excitation of Pd. We find evidence that Pd $3d_{3/2}$ core holes have only about a $(12\pm3)\%$ probability of undergoing a CK-preceded Auger decay, which is in line with previous estimates based on the core-level linewidths.

II. EXPERIMENTAL ASPECTS

All the experiments were carried out at beamline *U*16*B* of the VUV ring of the National Synchrotron Light Source at Brookhaven National Laboratory. The spectrometer is described in detail elsewhere[33–36] and features two cylindrical mirror analyzers (CMA's) that are aligned to look at the same spot on the sample which is illuminated with monochromated synchrotron radiation. To obtain an Auger coincidence spectrum one CMA remains fixed at a set kinetic energy corresponding to the peak of the intensity for a core-level photoelectron feature, and the second CMA is scanned through the kinetic-energy range of the associated Auger electron feature. To accommodate the time resolution of the analyzer, only electrons that are detected in the two CMA's within 20 ns (±10 ns) of each other are accepted as valid coincidence events. The coincidence counts accepted in this time period will include both true coincidence events, that is, those originating from the same excitation, as well as ''accidental'' coincidence events, those originating from different excitation events at different sites that fortuitously arrive at the analyzers ''simultaneously,'' i.e., within the ±10 ns analyzer width. The rate of the ''accidental'' coincidence events can be determined by taking a second delayed coincidence spectrum separated temporally from the first spectrum by long enough period to ensure that no true coincidence events will be counted. The true coincidence spectrum can then be obtained by subtracting the accidental spectrum from the initial coincidence spectrum. For comparison, a conventional noncoincidence (or ''singles'') photoemission spectrum is acquired along with the coincidence data.

Coincidence measurements were made of the Pd M_4VV and M_5VV Auger lines with an incident photon energy of 470 eV. The combined energy resolution, considering photon and electrons, was 0.72 eV and the spectra were acquired with an energy spacing of 0.5 eV between data points. Coincidence data was taken from a 3-monolayer Pd film deposited onto a ruthenium (0001) crystal. The Ru crystal was cleaned by repeated sputter (500 eV Ar^+ ions) and anneal cycles (1 h at 1000 °C in 5×10^{-5} Torr O_2, followed by a flash anneal to 1800 °C). Sample cleanliness was monitored *in situ* by soft x-ray photoemission spectroscopy. The films were deposited *in situ* using a well-outgassed, well-characterized, resistively heated evaporation source with a deposition rate of 1 ML/h. During deposition, the end chamber pressure did not rise above 6×10^{-10} Torr. Palladium grows in an epitaxial Pd(111) structure on this surface and our previous studies[37] have shown sharp low-energy electron-diffraction patterns for similar films. Although we are working with a thin film, the singles Auger spectrum is indistinguishable from that of a bulk Pd(111) sample. Furthermore, owing to the surface specificity of the APECS technique (it requires two electrons to escape from the surface, which considerably reduces the effective depth probed), a 3 ML film should well represent a bulk Pd(111) sample. Film cleanliness was again monitored with *in situ* soft x-ray

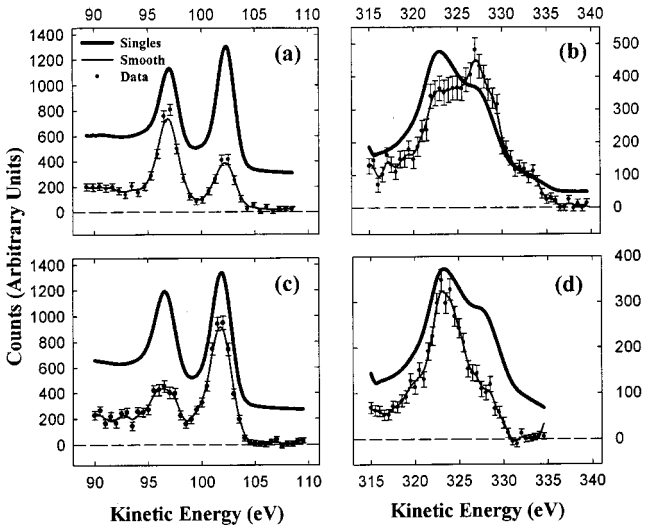

FIG. 1. APECS spectra of Pd. (a) The Pd $3d_{3/2}$ core-level spectrum taken in coincidence with Pd M_4VV Auger electrons ($E_{\text{fixed}}=328.5$ eV); (b) the Pd M_4VV taken in coincidence with the Pd $3d_{3/2}$ photoelectrons ($E_{\text{fixed}}=96.5$ eV); (c) the Pd $3d_{5/2}$ core-level spectrum taken in coincidence with Pd M_5VV Auger electrons ($E_{\text{fixed}}=323$ eV) and; (d) the Pd M_5VV Auger spectrum taken in coincidence with the Pd $3d_{5/2}$ photoelectrons ($E_{\text{fixed}}=102$ eV).

photoemission spectroscopy and the crystal was cleaned and films redeposited before oxygen contamination reached significant levels.

III. AS-ACQUIRED AND INTRINSIC AUGER LINE SHAPES

The as-acquired APECS spectra for the Pd M_4VV and M_5VV Auger lines and for the $3d_{3/2}$ and the $3d_{5/2}$ core levels are shown in Figs. 1(a)–1(d). In each figure, the singles and coincidence spectra are referenced to the same zero of counts. The singles spectra have been scaled to match the relevant APECS intensities. It can be observed immediately that the as-acquired APECS scans differ considerably from the conventional singles spectra. The coincidence intensity goes to zero above the high kinetic-energy edge of all the coincidence spectra. Furthermore, the M_5VV APECS spectrum reveals intensity at kinetic energies as high as 331 eV. In the singles spectrum, this emission is totally obscured by the M_4VV line. Regarding the M_4VV APECS spectrum, while the majority of the intensity lies between 325 and 336 eV, there is a pronounced shoulder between 320 and 325 eV. Some of this shoulder can be associated with the CK decay mentioned in the Introduction, but, as will be discussed below, most of it is M_5VV emission arising from coincidence with $3d_{5/2}$ photoelectrons that were inelastically scattered to a kinetic energy of 97 eV.

In previous studies focusing on Ag,[31,32] we have determined that the measurement of the M_5VV Auger spectrum in coincidence with the $3d_{5/2}$ core level directly determines the intrinsic line shape of the M_5VV transition. The $3d_{5/2}$ electrons are less tightly bound than those in the $3d_{3/2}$ level and are therefore emitted with a higher kinetic energy. As there

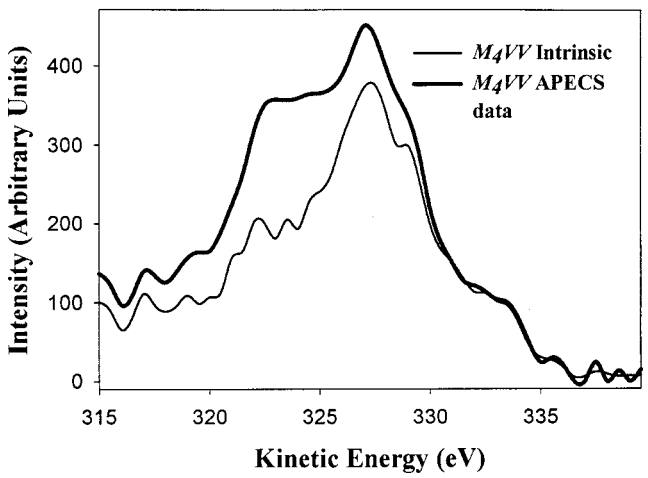

FIG. 2. The intrinsic line shape (thin curve) of the M_4VV Auger transition after the contribution from M_5VV Auger electrons has been removed. The as-acquired M_4VV APECS spectrum is also shown (heavy curve). The as-acquired line shape has a 25% contribution due to inelastically scattered $3d_{5/2}$ electrons.

are no significant mechanisms by which the $3d_{3/2}$ electrons can gain a large amount of kinetic energy ($\sim$5 eV for Pd), the probability for them to emerge from the solid in coincidence with the $3d_{5/2}$ photoelectrons is essentially zero. Therefore the as-acquired line shape of the M_5VV Auger spectrum is free from any contribution from the spin-orbit partner. The intrinsic M_4VV line shape is slightly more complicated to ascertain. If primary $3d_{5/2}$ photoelectrons lose energy by undergoing inelastic scattering within the solid, they can escape from the surface at the same kinetic energy as the primary $3d_{3/2}$ photoelectrons and contribute to the background under the $3d_{3/2}$ peak. The $3d_{5/2}$ core hole will then decay via a M_5VV Auger process and both the photoelectron and Auger electron will arrive at the detector simultaneously within the timing resolution of our spectrometer. This will lead to a contribution to the M_4VV Auger spectrum in the region of the M_5VV Auger peak. The magnitude of this contribution can be deduced from the APECS scan of Fig. 1(c), which was obtained in coincidence with Auger electrons with a kinetic energy of 323 eV. It is an easy matter[31,32] to fit this spectrum and determine that when one analyzer is set at 323 eV and the other at 97 eV, 25% of the coincidence emission is associated with $3d_{5/2}$ core holes. The identical coincidence conditions occur for the 323 eV point in the spectrum of Fig. 1(b), and therefore 25% of the coincidence emission at this energy is from M_5VV decays. As we know the intrinsic M_5VV line shape from Fig. 1(d), we can subtract the correct proportion of M_5VV emission from the as-acquired spectrum of Fig. 1(b) and generate the intrinsic M_4VV spectrum. Both the as-acquired and intrinsic M_4VV spectra are presented in Fig. 2.

IV. ANALYSIS OF THE Pd M_4VV AND M_5VV AUGER LINES

The CS framework investigates the nature of distortion produced by a Coulomb interaction of the two holes in the

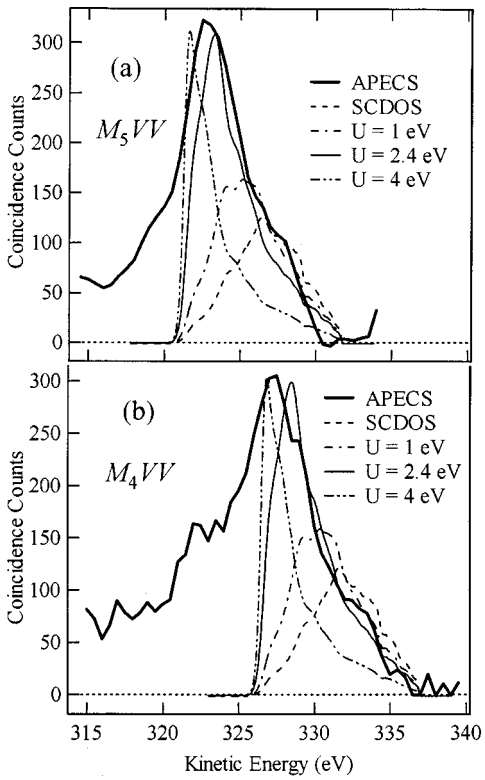

FIG. 3. Cini-Sawatzky distortions of a self-convolution of the Pd valence-band density of states (SCDOS) with various values of U, the valence-band hole-hole Coulomb interaction, for (a) the M_4VV and (b) the M_5VV Auger spectra.

final state of an Auger transition. The critical parameter of the theory is the ratio U/W, where U is the hole-hole Coulomb interaction energy and W is the width of the valence band. The CS distorted line shape will be either more bandlike or more atomic like depending on the magnitude of the ratio of U/W. In transition metals, W is usually taken to be the width of the d bands, which have a much higher DOS than the s,p bands. For a situation where U/W is $\ll 1$ (representative of a weak hole-hole interaction), the probability of coupling to the electronic bands is enhanced and the holes decay primarily by hopping away to neighboring sites. In this case, the Auger spectra will bear a close resemblance to the SCDOS.

As an initial attempt to model the Pd Auger line shapes, we consider a self-convolution of a calculated Pd valence-band density of states[38] and then distort it according to the CS transformation using different strengths of the Coulomb interaction between the two final-state valence-band holes. As outlined in Ref. 14, this line shape, which we will denote $\tilde{N}^0(E)$, is given by

$$\tilde{N}^0(E)=\frac{N^0(E)}{[1-UH(E)]^2+[\pi UN^0(E)]^2}, \qquad (1)$$

where $N^0(E)$ is the SCDOS of the calculated Pd DOS, $H(E)$ is the Hilbert transform of the SCDOS, and U is the Coulomb interaction between the two-hole final state. Given the density of states, then U is the only adjustable parameter.

TABLE I. Energy splitting of d^8 final-state multiplets relative to the most intense $^1G_4$ multiplet, the relative intensities of each multiplet for both the M_4VV and M_5VV Auger transitions, and the resultant Coulomb repulsion energy U for each multiplet configuration. The first three columns are from Weightmann *et al.*, Ref. 12. The U value for the $^1G_4$ configuration was experimentally determined and the U's for the other multiplets are rigidly shifted by the entries in the first column.

Multiplet	Energy splitting (eV)	M_4VV intensity	M_5VV intensity	Coulomb Energy U (eV)
$^0S_1$	−2.41	2.28	2.55	5.61
$^1\mathbf{G}_4$	**0**	**27.69**	**24.48**	**3.2**
$^1D_2$	0.22	21.38	5.92	2.98
$^3P_0$	0.3	5.43	3.20	2.9
$^3P_1$	0.32	8.89	5.91	2.88
$^3P_2$	0.73	7.57	14.47	2.47
$^3F_2$	1.33	9.45	9.13	1.87
$^3F_3$	1.49	14.89	10.06	1.71
$^3F_4$	1.89	2.42	24.28	1.31

Attempts to model the intrinsic M_5VV and M_4VV lines with the CS line shape, determined using different values of U, are presented in Figs. 3(a) and 3(b), respectively. In Figure 3 it can be seen that the distortions of the SCDOS for various values of U can provide reasonable descriptions of *parts* of each spectrum, but a consistent account of both spectra does not occur. The SCDOS gives a good account of the first few eV of both the M_4VV and M_5VV spectra, but does not explain the main intensity near the peak of each spectrum. The line shape given by $U=2.4$ eV gives a peak at about the correct energy for the M_5VV spectrum, but is too narrow. Also, this value of U gives a line shape that peaks at too high a kinetic energy compared to the M_4VV APECS spectrum. Finally, $U=4$ eV gives a line shape that is consistent with the maximum of the M_4VV data, but gives a poor description of the high kinetic-energy edge. In addition, when compared to the M_5VV APECS spectrum, this value of U gives a line shape that peaks at too low an energy. As can be seen from Fig. 3, applying the CS theory to the SCDOS using a single value of U cannot provide a consistent description of the Pd M_4VV and M_5VV Auger spectra.

The nature of the Pd $M_{45}VV$ Auger line shape in dilute alloys suggests that the strong peaks in the M_5VV and M_4VV spectra may have their origins in atomic multiplets.[7–9,11,12,19,24–26,28] When $U/W\gg 1$, strong hole-hole correlations produce sharp atomiclike features in the spectra with energy splittings and intensities determined by atomic multiplet configurations of the two-hole final state. Owing to screening of the core hole, it is appropriate to consider a Pd d^8 configuration to describe the Auger final state.[24,26] The energy splitting of the different Pd d^8 multiplet components, and their intensities for coupling to $3d_{3/2}$ and $3d_{5/2}$ core holes, as calculated by Weightman *et al.*[12] are shown in Table I. These results are from Hartree-Fock calculations that

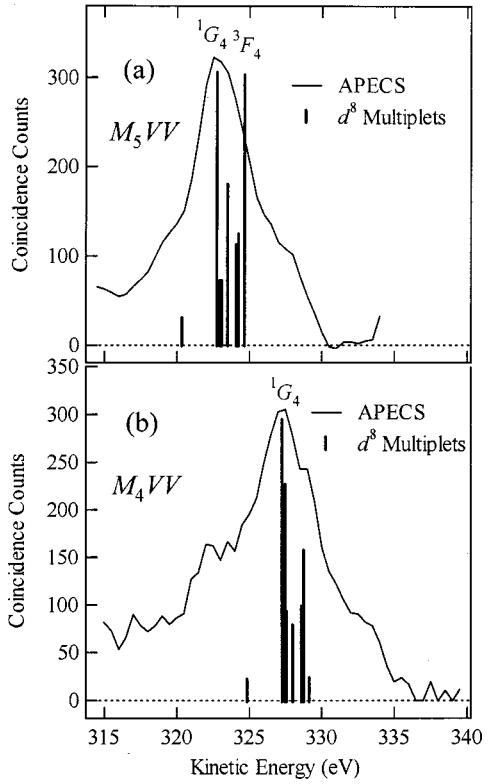

FIG. 4. Comparison of the Pd d^8 final-state multiplets (heavy bars) with (a) the Pd M_4VV, and (b) the Pd M_5VV APECS spectra. The most intense multiplet, the $^1G_4$, has been aligned with the most intense part of each spectrum.

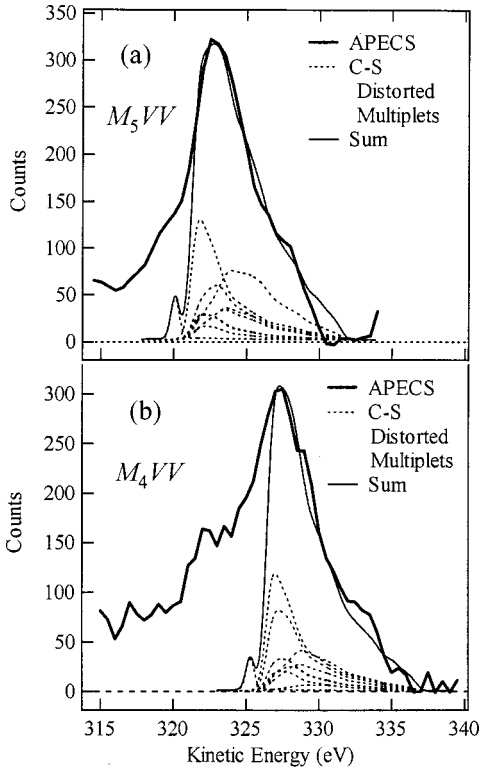

FIG. 5. Individual Cini-Sawatzky distorted final-state multiplets from Ref. 12 for a d^8 final state along with their sum, compared with (a) the Pd M_4VV and (b) the Pd M_5VV APECS spectra. The value of on-site Coulomb interaction for the most intense $^1G_4$ multiplet is 3.2 ± 0.1 eV.

were carried out using the relevant Slater integrals and intensities based on the *jj*-intermediate coupling scheme[39] and using values of the radial integrals given in the literature.[40] The splitting has been reduced by 20% to account for the neglect of relativistic corrections in the self-consistent field calculations. The individual multiplet lines are plotted along with the M_5VV and M_4VV APECS scans in Figs. 4(a) and 4(b), respectively. The most intense multiplet, the $^1G_4$, has been aligned with the most intense part of the Auger APECS scans. Once again, this model poorly describes the APECS spectra. For both Auger transitions, the intensity of the main peak is reasonably well accounted for, but the total width of the multiplet envelope is much narrower than the measured Auger features. For the M_5VV APECS transition, the comparison is particularly unfavorable because the $^3F_4$ multiplet overestimates the intensity at the high kinetic-energy edge of the spectrum. Furthermore, the high kinetic-energy edge, which was somewhat accounted for by the SCDOS, is totally absent in this pure multiplet description.

An understanding of these line shapes can be ascertained by using an extension of the CS theory that we employed earlier to understand the intrinsic line shapes of the M_4VV and M_5VV transitions in Ag.[31,32] In this approach, each multiplet of the two-hole final state can be considered as having its own value of U in the CS theory and therefore each will have a different amount of distortion. The difference between the value of U for each multiplet component is taken as the multiplet splitting given by the atomic calculation.[12] The shape of the spectrum is then fixed by choosing U for one of the multiples, we chose the intense $^1G_4$ term, which is the only adjustable parameter in the fit. Once again, we use the relative energies and intensities of each component[12] given in Table I.[41] The overall line shape is the sum of the distorted line shapes of each of the individual multiplet components.

The results showing all of the individual multiplet components as well as their sum compared to the M_5VV and M_4VV APECS scans can be seen in Figs. 5(a) and 5(b), respectively. To account for instrumental and lifetime broadening, the individual lines were convolved with a Gaussian profile of 1.3 eV full width at half maximum. As can be seen, a value of $U=3.2\pm0.1$ eV for the $^1G_4$ final state provides a very good description of both the M_4VV and M_5VV APECS scans. The resulting values of U for the other multiplet components are given in Table I. In Figs. 6(a) and 6(b), a simple integrated background[31,32] has been added to the sum of the individual distorted multiplet components in order to account for the inelastic contribution to the line shape. Although the fit could probably be improved with the addition of a more sophisticated background, both spectra exhibit emission in excess of this background, which is intrinsic in origin, on the low kinetic-energy side of the main peak. This emission may be due to multiple electron decay events or a discrete energy-loss mechanism such as surface plasmon excitation. In the M_4VV spectrum, the excess emission accounts for a larger fraction of the spectral weight, and extends for a larger en-

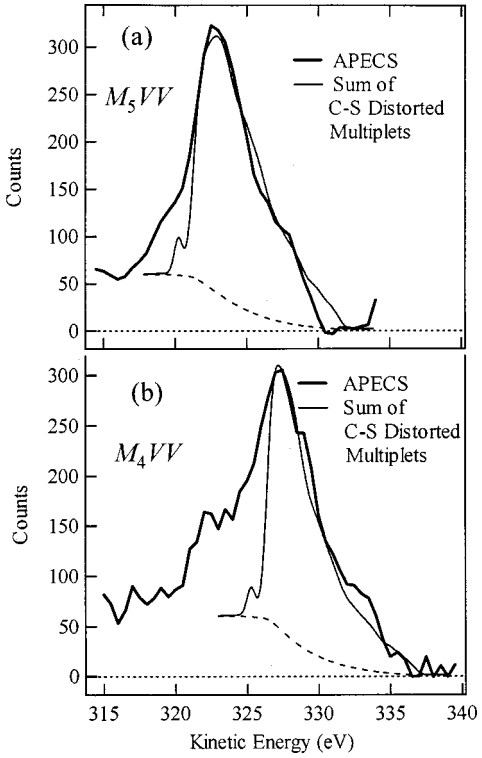

FIG. 6. The (a) Pd M_4VV and (b) Pd M_5VV Auger spectra (heavy curves) compared to the sum of the Cini-Sawatzky distorted final-state multiplets (thin curve) added to a simple inelastic background (dashed curve).

ergy range, than in the M_5VV line. This additional M_4VV emission is attributed to the CK transition as mentioned in Sec. I. In Fig. 7, the two APECS spectra have been added together and compared to the $M_{45}VV$ singles spectrum. The best fit is obtained with an M_5VV to M_4VV ratio of $\approx$1.0:0.7, which is in excellent agreement with the ratio of 1.0:0.69 expected from theory.[12] The origin of the difference between the present measurements and those of Weightman is not entirely clear; however it may arise from the fact that Weightman's work was on dilute Pd alloys and we are looking at elemental Pd. This would suggest that alloying may change the probability of CK-preceded Auger transitions.[38]

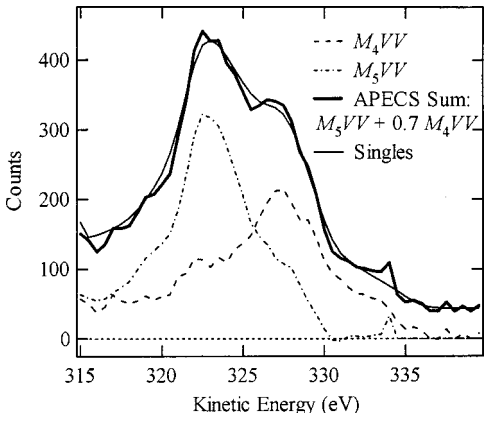

FIG. 7. Sum of the intrinsic M_4VV and M_5VV APECS spectra, summed in the ratio 1: 0.7, compared to the singles Auger $M_{45}VV$ spectrum.

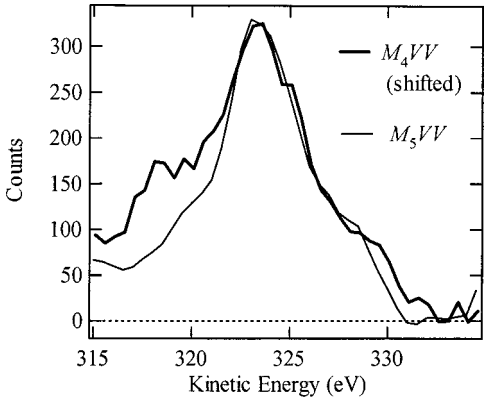

FIG. 8. The intrinsic Pd M_4VV (heavy curve) and M_5VV (thin curve) spectra. The M_4VV spectrum has been scaled and shifted in energy to align the main peaks in the two spectra and to compare the low kinetic-energy region where contributions from a Coster-Kronig transition are expected (around 318 eV). A comparison of the area under each curve in this region suggests a CK contribution to the M_4VV spectrum of around $(12\pm3)\%$, in good agreement with values quoted in the literature (Ref. 30).

Recently, Creagh and Thurgate[29] reported an APECS study to independently determine the M_4VV and M_5VV Auger line shapes. As described in Sec. I, they attributed the substantial excess Auger emission observed in the energy range of the M_5VV line but in coincidence with $3d_{3/2}$ photoelectrons to the CK-preceded decay. However, as we discussed in the description of Fig. 2, the contribution of inelastically scattered $3d_{5/2}$ photoelectrons to the $3d_{3/2}$ photoelectron peak intensity must be removed from the as-acquired M_4VV APECS spectrum before the intrinsic line shape can be determined.

To estimate the CK contribution to the intrinsic M_4VV spectrum, we shift the M_5VV spectrum to lower energy by 4.4 eV (an amount less than the 5.5 eV core level separation because the peak in the M_5VV spectrum does not coincide with the peak of the $^1G_4$ multiplet) so as to line up the peaks in both spectra, as shown in Fig. 8. As the direct Auger decay spectra, along with their inelastic parts, are expected to be similar in this region, the difference in total intensity in the M_4VV line can be attributed to a CK transition. The ratio of the excess M_4VV intensity between 315 and 322 eV to the total M_4VV intensity suggests that the probability that a Pd $3d_{3/2}$ core hole decaying via a CK transition is on the order of $(12\pm3)\%$. This value agrees well with the results of Mårtensson and Nyholm[30] obtained by comparing the core level Pd $3d_{3/2}$ and $3d_{5/2}$ photoelectron transition widths.

V. CONCLUSIONS

We have performed a high-resolution APECS study of the Pd M_4VV and M_5VV Auger transitions and produced the intrinsic Auger line shapes for both transitions. We have produced good agreement between experiment and fits to the data using a CS distortion of the d^8 final-state multiplets with an onsite Coulomb interaction for both Auger transitions of

3.2 ± 0.1 eV for the most intense $^1G_4$ multiplet, suggesting that the CS framework can be applied successfully to simple ''open-shell'' systems. We find $\sim(12 \pm 3)\%$ of the intrinsic M_4VV intensity is associated with a Coster-Kronig decay of the $3d_{3/2}$ core hole, a rate that agrees well with that predicted by studies of the Pd $3d$ core-level spectra.[30]

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*Present address: Condensed Matter and Thermal Physics Group MST-10, Los Alamos National Laboratory, Mailstop K-764, Los Alamos NM 87545.

†Corresponding author: bart@physics.rutgers.edu

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