Line shape of the Ag $M_{4,5}VV$ Auger spectra measured by Auger-photoelectron coincidence spectroscopy

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We present high resolution Ag M_5VV and M_4VV Auger spectra obtained in coincidence with $3d_{5/2}$ and $3d_{3/2}$ core photoelectrons, respectively. Auger photoelectron coincidence spectroscopy (APECS) was used to separate these overlapping Auger lines and determine the intrinsic line shape of each spectrum. As the on-site Coulomb correlation energy U of Ag is comparable to twice the $4d$ bandwidth, $2W$, (i.e., $U/2W\sim1$), the coincidence Auger spectra exhibit both atomiclike and bandlike character. We find that whether considered separately or in combination, neither bandlike nor atomiclike line shapes give a satisfactory account of these Auger spectra. Instead, the intrinsic Ag M_5VV and M_4VV line shapes are well described by the Cini-Sawatzky theory when it is applied separately to each component of the multiplet structure of the $4d^85s^2$ Auger final state. A fit to the APECS data indicates that the correlation energy the $^1G_4$ multiplet is 4.8 ± 0.1eV. Furthermore, our analysis indicates that the missing intensity in the vicinity of the $^3F_4$ multiplet in the Ag M_5VV Auger line, which has been noted in previous studies, results from a shift in the spectral weight of this multiplet component to higher kinetic energy, into the bandlike region of the spectrum.

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I. INTRODUCTION

The line shape of the $M_{4,5}VV$ Auger spectrum of Ag has been controversial for many years[1–9] because it represents an intermediate situation. Metals whose properties are well described within the independent-electron approximation such as Al, exhibit a so-called bandlike core-valence-valence (CVV) Auger spectrum.[1] In this case, the Auger-line shape is closely related to the self-convolution of the valence band density of states (SCDOS). On the other hand, for metals such as Cu, which have a large on-site Coulomb interaction of the final state holes in the d bands, the CVV Auger spectrum has an atomic character as evidenced by the sharp features of the Auger line profile.[10] The prominent features in the Cu CVV Auger spectra are indicative of multiplet splitting in the two-hole final state. Whether a metal exhibits an atomiclike or bandlike CVV Auger-line shape depends on the ratio of the hole-hole interaction energy U to twice the one-electron valence bandwidth $2W$. When the hole-hole interactions are weak, i.e., $U/2W\ll1$, the Auger spectrum resembles the SCDOS. For strong hole-hole correlations, $U/2W\gg1$ and the spectrum is atomiclike with a strong multiplet structure.

Ag is an interesting case as $U/2W\sim1$ and the detailed nature of the line shape is less obvious. Early studies by Powell[1] noted that the line shape of the $M_{4,5}VV$ Auger spectrum of solid Ag closely resembles that of gas phase Ag (Refs. 2–4) in that it has sharp M_4VV and M_5VV features, a shift of spectral weight away from the M_4 and M_5 subshell binding energies, and the presence of additional structure in the Auger-line profiles. Burkstrand and Tibbets[5] questioned this interpretation and argued that the Ag line shape could be accounted for by a bandlike spectrum with a constant energy correction to account for Coulombic interaction and relaxation effects and different matrix elements for two-hole final states with varying symmetries. Their argument was in turn challenged by Matthew,[6] who noted, among other observations, that the ideas of Burkstrand and Tibbets predict the same line shape for Ag M_4VV and M_5VV Auger peaks, in contradiction to observations. Furthermore, the relatively large energy correction of 5.0–5.8 eV introduced by Burkstrand and Tibbets implied a large degree of localization and hence a significant atomiclike character of the Ag $M_{4,5}VV$ spectrum. In a subsequent high-resolution study of the Ag $M_{4,5}VV$ line, Parry-Jones, Weightman, and Andrews[7] concluded that the spectrum contained both components; an atomic multiplet dominates the line, but there is a bandlike contribution estimated to be about 12% of the atomic part for the M_4VV Auger transition. The authors further commented that for a system where $U/2W$ is close to unity, this fraction is surprisingly small. However, their analysis was complicated by the large overlap between the M_4VV and M_5VV lines. Recently, Lund and Thurgate addressed these questions in a study of the Ag $M_{4,5}VV$ Auger lines using Auger-photoelectron coincidence spectroscopy (APECS).[8,9] By obtaining the $M_{4,5}VV$ Auger line in coincidence with emission from the $3d_{5/2}$ core level, they measured the intrinsic Ag M_5VV spectrum and found evidence for the bandlike emis-

sion that was about 19% of the atomic part. Unfortunately, the resolution of their instrument limited their ability to comment further on the line shape of either Auger transition. Thus, a reexamination of the Ag $M_{4,5}VV$ Auger spectra and a reinterpretation of the Auger-line shapes is in order to resolve some of these outstanding issues.

In this paper, we report the results of a high resolution APECS study of the Ag M_4VV and M_5VV Auger spectra using synchrotron radiation as the excitation source. We have obtained Ag M_5VV and M_4VV Auger spectra in coincidence with the primary emission from the $3d_{5/2}$ and $3d_{3/2}$ core levels, respectively. An APECS measurement of the Ag M_5VV Auger line directly reveals the intrinsic line shape of the Auger transition while the intrinsic M_4VV Auger line shape can be determined from the APECS measurements of the M_4VV Auger line and the $3d_{5/2}$ and $3d_{3/2}$ core levels.[11] Our analysis indicates that the classification of Auger spectra as atomic or bandlike can be misleading. A many-body model of Auger transitions developed independently by Cini[12,13] and Sawatzky[14] describes the continuous transformation of Auger-line shapes from a simple bandlike SCDOS to strongly atomiclike as $U/2W$ becomes large. We therefore analyze the intrinsic M_5VV and M_4VV Auger-line shapes within the framework provided by the Cini-Sawatzky theory. With this model, we are able to accurately describe the intrinsic Auger line shapes as measured with APECS provided that each multiplet of the $4d^8 5s^2$ final-state configuration has a different, but well-defined value of U.

II. EXPERIMENTAL ASPECTS

All of the data reported here were acquired at beamline U16B of the National Synchrotron Light Source at Brookhaven National Laboratory. Synchrotron radiation from the VUV storage ring is dispersed by a monochromator and focused to a small spot on the sample. The spectrometer, which is described in detail elsewhere,[15] has two cylindrical mirror analyzers (CMA's) that are aligned to the illuminated spot. To obtain the coincidence Auger spectra described here, one CMA remained at a fixed kinetic energy corresponding to the peak of the core photoelectron spectrum while the second CMA scanned kinetic energy through the associated Auger spectrum. To accommodate the time resolution of the analyzer, electrons that are detected in the two CMA's 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 obtained. The true coincidence spectrum, which is what we present here, is obtained by subtracting the accidental spectrum from the total coincidence spectrum. For comparison purposes, a conventional, noncoincidence (also called singles) photoemission spectrum is acquired along with the coincidence data.

Coincidence measurements of the Ag M_4VV and M_5VV Auger lines were acquired from a Ag(100) crystal at $h\nu = 470$ eV. The energy resolution was 0.72 eV (photons+electrons) and the spectra were acquired with an energy spacing between data points of 0.25 eV. The sample was known to produce sharp low energy electron diffraction and Laue x-ray diffraction patterns. The sample was cleaned by repeated cycles of sputtering (500-eV Ar^+ ions) and annealing (740 K for 15 mins). Sample cleanliness was monitored *in situ* with soft x-ray photoemission spectroscopy. The cleaning cycles were repeated until no contamination could be detected. Coincidence data were acquired after the sample had returned to room temperature.

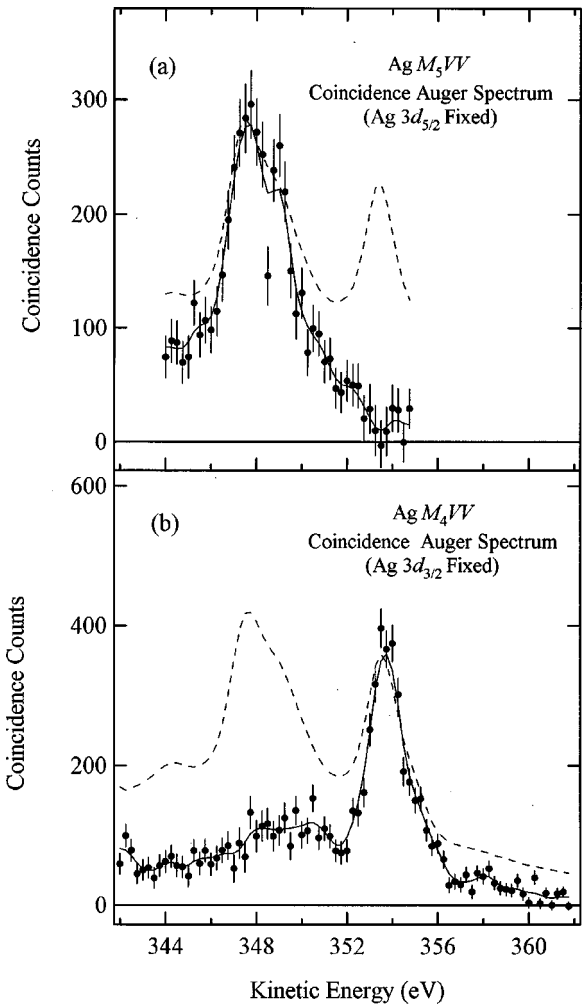

FIG. 1. High energy resolution APECS spectra of the (a) Ag M_5VV and (b) Ag M_4VV Auger transitions obtained in coincidence with Ag $3d_{5/2}$ and $3d_{3/2}$ core photoelectrons, respectively. The photon energy was 470 eV. In both panels, the filled circles with error bars are the coincidence data, the solid black line is the smoothed coincidence data, and the dashed lines are the singles spectra.

III. AS-ACQUIRED AND INTRINSIC AUGER-LINE SHAPES

Figure 1(a) presents the Ag M_5VV Auger line measured in time coincidence with Ag $3d_{5/2}$ core photoelectrons while Fig. 1(b) presents similar data for the Ag M_4VV Auger spectrum measured in coincidence with electrons at the kinetic energy of the primary emission from the Ag $3d_{3/2}$ core level. In both the spectra, the filled dots with error bars are the

coincidence counts, the solid black line is a smoothed version of the raw data, and the dashed line is the singles (conventional) spectrum. The singles and the coincidence spectra are referenced to the same zero level and the singles spectra have been scaled to match the APECS intensities for the M_5VV line in Fig. 1(a) and the M_4VV Auger line in Fig. 1(b). Several important features are common to both the M_5VV and M_4VV coincidence Auger spectra. First, the coincidence counts drop to zero at high kinetic energies above the main peaks indicating that the background of inelastically scattered electrons is eliminated in an APECS measurement at kinetic energies above the range of allowed Auger electron energies. Second, at kinetic energies below the main peak, the background is also considerably reduced. Finally, in both spectra, the contribution from the overlapping Auger line of the spin-orbit partner is either eliminated or reduced considerably.

In a recent analysis,[11] we determined that the measurement of the Ag M_5VV Auger spectrum in coincidence with emission from the Ag $3d_{5/2}$ core level directly determines the intrinsic line shape of the Ag M_5VV Auger transition. The electrons in the $3d_{5/2}$ level are less tightly bound than the $3d_{3/2}$ electrons and thus are photoemitted at a higher kinetic energy. As there are no significant mechanisms by which $3d_{3/2}$ photoelectrons can gain large amounts of kinetic energy ($\sim$6 eV), the probability of an electron from the $3d_{3/2}$ level emerging from the solid at the same kinetic energy as primary $3d_{5/2}$ photoelectrons is essentially zero. Therefore, the shape of the Ag M_5VV Auger line as measured with APECS is free of any contribution from the spin-orbit partner M_4VV level. As seen in Fig. 1(a), the line shape is characterized by a strong peak at 347.5 eV. At energies above the peak, there is a pronounced shoulder at 349 eV. In addition, there is a considerable intensity extending from 350 eV up to about 355 eV, which is the highest energy measured for the M_5VV line in these experiments. A coincidence measurement is required to view this high kinetic energy portion of the M_5VV Auger line in Ag as much of it lies in the same region as the emission from the M_4VV Auger line. At kinetic energies below the main peak of the M_5VV line, the intensity drops below the low-energy background in the singles data. APECS data for the Ag M_5VV Auger level measured over a wider energy scale (not shown) indicate that the coincidence counts drop to zero on the high kinetic-energy side of the main peak by 357 eV. Furthermore, the background at energies $\sim$10 eV below the main peak is reduced approximately by a factor of 2 with respect to the singles spectrum.[11]

The as-acquired coincidence spectrum for the Ag M_4VV Auger line, which is presented in Fig. 1(b) is similarly characterized by a single peak although the peak occurs at 353.5 eV due to the increased binding energy of the Ag $3d_{3/2}$ core level. The Ag M_4VV Auger peak is somewhat narrower than the M_5VV Auger line. Also, the high kinetic energy portion of the M_4VV Auger line, which extends from approximately 356 eV up to 362 eV is smaller than the corresponding high energy portion of the M_5VV line.

Determining the intrinsic line shape of the Ag M_4VV Auger transition is slightly more complicated than arriving at the intrinsic shape of the M_5VV transition. The kinetic energy of Ag $3d_{3/2}$ photoelectrons is less than that of primary $3d_{5/2}$ photoelectrons. Therefore, a portion of the background under the main peak of the Ag $3d_{3/2}$ core level spectrum contains $3d_{5/2}$ photoelectrons that have lost energy via inelastic scattering processes before exiting the solid. The remaining $3d_{5/2}$ core hole decays via an M_5VV Auger transition. The inelastically scattered $3d_{5/2}$ photoelectron and the M_5VV Auger electron will emerge from the crystal simultaneously (within the timing resolution of our spectrometer). Therefore, their detection in a coincidence measurement will lead to a contribution to the M_4VV Auger spectrum in the vicinity of the M_5VV Auger peak at 347.5 eV. Fortunately, the amount of this contribution can be assessed by measuring the Ag $3d_{3/2}$ and $3d_{5/2}$ core-level spectra in coincidence with the emission from the M_4VV Auger level.[11] This, rather small, contribution from M_5VV Auger electrons can then be removed from the as-acquired M_4VV Auger spectrum to generate the intrinsic line shape of the Ag M_4VV Auger transition. The results of this correction to the M_4VV Auger line are shown in Fig. 2. As seen in the figure, the amount of the correction is small and the difference between the as-acquired spectrum and the corrected spectrum is limited to a small reduction in intensity between 346 and 351 eV. The shape of the main peak is unaffected by the correction to the line shape.

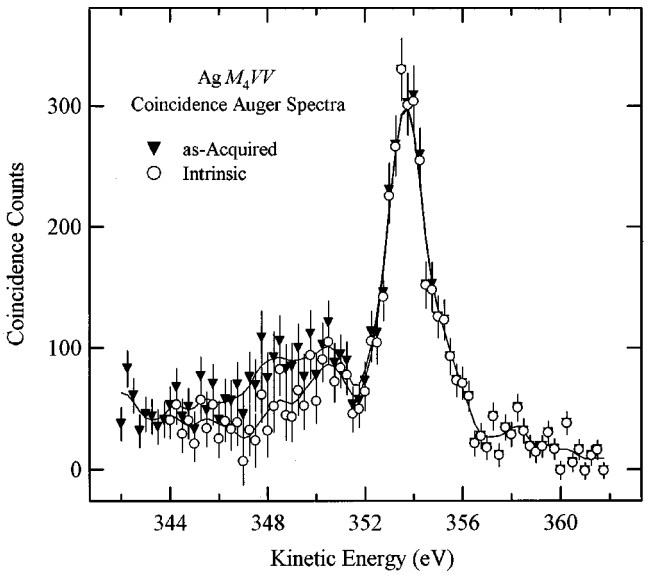

FIG. 2. As-acquired (filled triangles) and intrinsic (open circles) coincidence Ag M_4VV spectra. The latter is produced by removing the M_5VV contribution to the as-acquired M_4VV spectrum using the procedure described in Ref. 11.

IV. ANALYSIS OF THE Ag M_5VV AND M_4VV AUGER LINES

To model the Ag Auger line shapes, we used an empirically derived density of states (DOS) based on the high resolution ultraviolet photoemission spectroscopy (UPS) spectrum of the Ag(100) valence band shown in Fig. 3(a). The spectrum was acquired at $h\nu = 50$ eV. The total energy

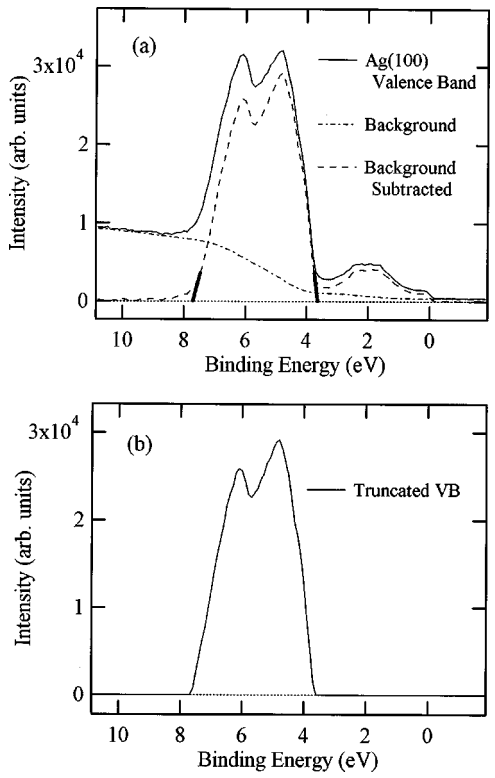

FIG. 3. Empirical Ag *d* DOS derived from experimental valence band photoemission spectrum of Ag(100). (a) Ag(100) valence band spectrum acquired at $h\nu = 50$ eV (solid line), Tougaard-type integrated background (dash-dotted line), background-subtracted data (dashed line), and truncation (heavy solid lines). (b) Resulting empirical Ag 4*d* DOS used for Ag M_5VV and M_4VV line shape calculations.

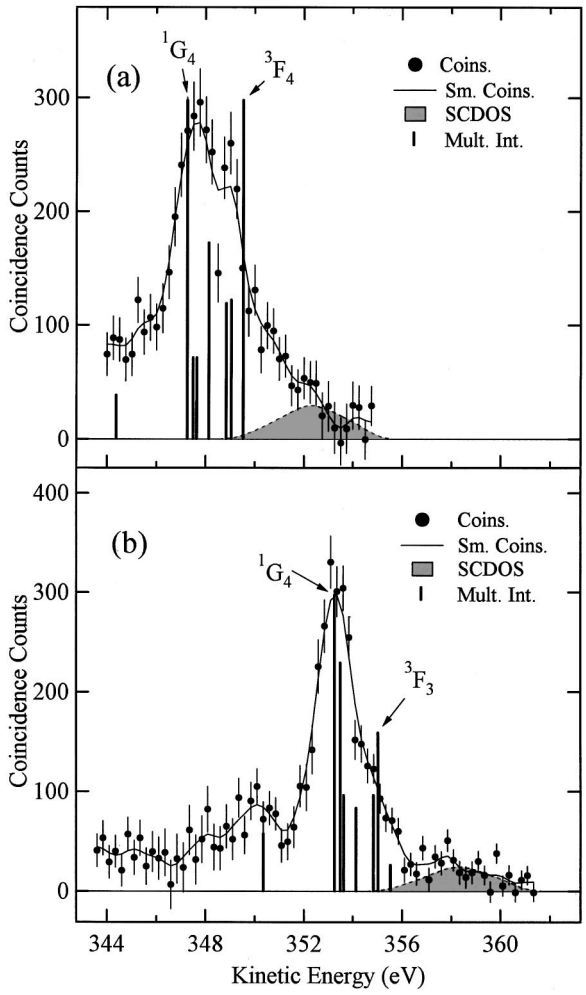

FIG. 4. Comparison of (a) the Ag M_5VV and (b) the Ag M_4VV coincidence Auger spectra (data points with error bars) with the Ag d^8 atomic multiplets (heavy vertical bars) and the SCDOS of the Ag *d* DOS from Fig. 3(b) (shaded regions). The principal multiplets for each Auger line are labeled.

resolution (photons+electrons) used to obtain the spectrum was 0.12 eV. For Ag, as with most late transition metals, the matrix elements for the $M_{45}N_{45}N_{45}$ Auger transitions are at least an order of magnitude larger than any other $M_{45}VV$ channel.[16] In our calculation of the line shape, therefore, we use a truncated DOS that preserves the shape of the *d* band but eliminates the minor *sp* contribution. Our method for arriving at this truncated DOS is shown in Fig. 3(a). First we subtract an integrated background [dash-dotted curve in Fig. 3(a)], which is generated with the method described by Tougaard and Kraaer[17] from the as-acquired UPS spectrum. We then extrapolate a straight line from the steepest part of the *d* bands down to zero intensity [heavy solid curves in Fig. 3(a)]. The intensity of all other emission outside this window was set to zero. The resulting DOS is shown in Fig. 3(b). We used this truncated DOS to generate the (SCDOS) and in all further computations of the Ag $M_{4,5}VV$ Auger lines.

The fact that both atomiclike and bandlike characteristics occur in the M_5VV and M_4VV Auger spectra can be seen in the coincidence data presented in Figs. 4(a) and 4(b), respectively. In both the panels, the shaded area is the SCDOS shifted by the binding energy of the respective initial state core hole. The intensity of the SCDOS in each panel has been adjusted to coincide with the approximate intensity of the APECS data in the bandlike portion of the Auger line. As can be seen in this figure, the SCDOS can account for most, but not all of the high-energy portion of the coincidence spectra.

Also shown in Fig. 4 are vertical solid lines that represent the energies and relative intensities of the atomiclike multiplet configurations for the two-hole final state in the M_5VV [Fig. 4(a)] and M_4VV [Fig. 4(b)] Auger lines. The energy of the multiplet was adjusted so that the most intense multiplet lines coincide with the peaks in the Auger spectra. The energy splittings and relative intensities were calculated by Parry-Jones, Weightman, and Andrews[7] based on Hartree-Fock atomic calculations of the $4d^85s^2$ final state with empirically determined Slater integrals while the relative intensities are based on *jj* coupling. To fit their experimental data, Parry-Jones, Weightman, and Andrews reduced the splitting from the atomic result by 20%. They did not attribute this to solid-state effects, but rather to the neglect of relativistic corrections in the self-consistent field calculations.[7] Their re-

TABLE I. Final state configurations for Ag M_4VV and M_5VV Auger transitions (column *A*), energy splittings (column *B*), relative intensities (columns *C* and *D*), and hole-hole correlation energies (column *E*). The values for the energy splittings and intensities in columns *B*, *C*, and *D* are relative to the M_5VV $^1G_4$ component and are taken from Ref. 7.

(*A*) Multiplet component	(*B*) Relative energy (eV)	(*C*) M_5VV Intensity	(*D*) M_4VV Intensity	(*E*) Hole-hole correlation energy (eV)
$^1S_0$	−2.89	0.13	0.22	7.7
$^1G_4$	0.00	1.00	1.14	4.8
$^1D_2$	0.24	0.24	0.88	4.6
$^3P_0$	0.37	0.11	0.09	4.4
$^3P_1$	0.38	0.24	0.37	4.4
$^3P_2$	0.88	0.58	0.32	3.9
$^3F_2$	1.59	0.40	0.37	3.2
$^3F_3$	1.78	0.41	0.61	3.0
$^3F_4$	2.28	1.00	0.10	2.5

sults are reproduced in columns *B*, *C*, and *D* of Table I. All values are given relative to the dominant $^1G_4$ component of the multiplet.

As can be seen in Fig. 4, neither the noninteracting holes approach nor the multiplet picture can independently provide an adequate description of the Auger line shape in Ag. While the bandlike interpretation does account for a substantial portion of the broad intensity above the main peak, the SCDOS is centered at far too high an energy to account for the main peak. Moreover, the SCDOS is broader than either the M_5VV or the M_4VV Auger line. On the other hand, the multiplet structure can account for the peak intensity in both Auger lines. However, the intense $^3F_4$ multiplet line in the M_5VV spectrum overestimates the high kinetic-energy edge of the M_5VV peak as has been noted in previous studies of the Ag $M_{4,5}VV$ Auger spectrum.[1,7,18] More fundamentally, this atomiclike approach fails to account for the broad intensity in the energy region appropriate to the SCDOS. Clearly, the M_5VV and M_4VV line shapes in Ag contain significant contributions that can be attributed to both of these descriptions.

An alternative approach to understanding these line shapes is offered by the Cini-Sawatzky (CS) theory, which we used to fit our APECS data for the Ag M_5VV and M_4VV Auger lines. The advantage of the CS theory is that it provides a continuous bridge from the bandlike case to the atomiclike case.[12–14] The CS distorted line shape will be either more atomiclike or more bandlike depending on the magnitude of the hole-hole interaction *U*. In this approach, each component of the Ag d^8 multiplet has a different value of *U* and thus a different amount of distortion. However, the relative splitting of the multiplet components is not arbitrary, but rather is fixed by the atomic calculation.[7] Therefore, in our fit we varied only the energy of the intense $^1G_4$ multiplet component and kept the relative energy of the other components fixed at the values determined by Parry-Jones, Weightman, and Andrews.[7] The relative intensities of each component, which were also taken from the calculations in Ref. 7, are determined by the transition rates between the initial and final states and the multiplicities of the final states.[16] The overall line shape is the sum of the distorted line shape for each component.[19]

The line shapes of the different two-hole final states corresponding to the various multiplet components of the Ag M_5VV and M_4VV Auger spectra were calculated using Eq. 14 of Ref. 13 [or the equivalent Eq. (13) of Ref. 20], which is reproduced here for convenience

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

In the above expression, $\tilde{N}^0(E)$ is the Cini-Sawatzky distorted Auger line shape, $N^0(E)$ is the SCDOS of the empirically-derived Ag DOS in Fig. 3(b), $H(E)$ is the Hilbert transform of the SCDOS, and *U* is the Coulomb interaction energy of the two-hole Auger final state. The spectral weight of each component was scaled by the multiplet inten-

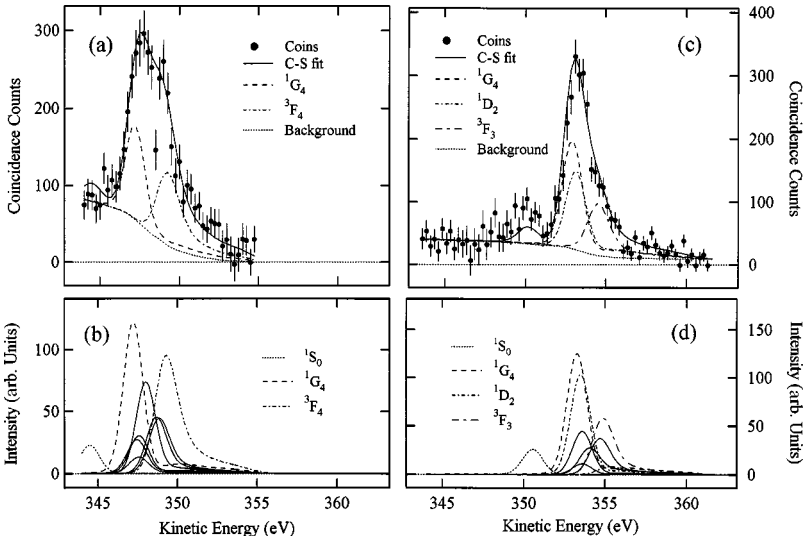

FIG. 5. (a) Fit (solid line) to the intrinsic Ag M_5VV APECS spectrum from Ag(100) generated by the sum of Cini-Sawatzky line shapes for each atomic multiplet lines of the Ag d^8 configuration. The two principle lines are shown as the dashed and dot-dashed curves, and the dotted line is the assumed background. (b) The calculated line shapes for each individual multiplet component. The fit assumes an interaction energy of the two holes in the Auger final state for the $^1G_4$ multiplet component of 4.8 eV for both Auger lines. (c) Same as (a) but for the Ag M_4VV transition. (d) Same as (b) but for the Ag M_4VV transition.

sities shown in Table I. The results are presented in Fig. 5(a) for the Ag M_5VV line and Fig. 5(c) for the M_4VV line. The overall fits, shown as the solid black lines in Figs. 5(a) and 5(c), are the sums of the nine weighted multiplet components plus an estimated inelastic background. Figures 5(b) and 5(d) show the CS distorted individual multiplet lines for the M_5VV and M_4VV transitions, respectively. The principal multiplet components are labeled in each figure. To account for instrumental resolution and lifetime effects, the lines for the individual components were broadened by convolving the lines with a Gaussian profile with a full width at half maximum (FWHM) of 1.40 eV. The fit was rather sensitive to the amount of broadening, and the fidelity of the fit to the data suffered if the broadening varied by more than $\pm$ 0.05 eV. A simple integrated background, shown as the dotted line in the upper two panels of the figure, was generated for both Auger lines to account for the inelastic contribution to the intrinsic line shape.

For both the M_5VV and the M_4VV lines, the best fit was given by $U=4.8\pm0.1$ eV for the $^1G_4$ final state and an overall width of the multiplet of 5.17 eV. As previously mentioned, the energies of the other components relative to the $^1G_4$ final state are presented in column *E* of Table I. The width of the multiplet is essentially the same as that used by Parry-Jones, Weightman, and Andrews.[7] The value of *U* determined in our experiments compares well with previously published results for the apparent hole-hole interaction energy $U_{\rm eff}$. $U_{\rm eff}$ is the difference between the peak position in the measured Auger spectrum and the peak in the SCDOS. In general, $U_{\rm eff}$ will be larger than *U*, but the difference between the two values will approach zero for $U\gg 2W$.[21] Using this definition, Powell[18] reports an estimated $U_{\rm eff}$ of 5.0 eV based on the peak position of the AgM_5VV Auger line, which is equivalent to assigning this $U_{\rm eff}$ to the $^1G_4$ component as this multiplet contributes most of the spectral weight at the peak, while Parry-Jones, Weightman, and Andrews estimate that $U_{\rm eff}$ is 5.1 eV for the $^1G_4$ component.[7] So, despite the fact that $U/2W\sim 1$ for Ag, we find that $U\sim U_{\rm eff}$.

V. DISCUSSION

We first discuss the fit of the M_5VV data, which is presented in Fig. 5(a). The overall fit reproduces almost all the details of the M_5VV data. The CS theory accounts for the width, intensity, and overall line shape of the peak quite well. The low kinetic-energy edge and the maximum intensity of the data closely coincide with the predicted line shape. The maximum of the overall M_5VV peak is close to the peak of the intense $^1G_4$ two-hole final state, but the experimental curve is peaked at about 0.5 eV higher kinetic energy than the calculated $^1G_4$ curve because all of the multiplets except the $^1S_0$ term contribute intensity at higher kinetic energies. In addition, the contribution from the intense $^3F_4$ final state at about 349.3 eV agrees very well with the high kinetic-energy edge of the main peak. The comparison between the $^1G_4$ and the $^3F_4$ components [dashed and dash-dotted curves, respectively, in Figs. 5(a) and 5(b)] is interesting as they both have the same integrated intensity (see column *C* of Table I), but the CS distorted line profiles are quite different. For the $^1G_4$ two-hole final state, we estimate that $U/2W$ is about 0.8 and thus the line shape has a strong atomiclike character with a residual bandlike part at higher kinetic energy. In contrast, the $^3F_4$ component has an estimated ratio $U/2W$ of about 0.4 and therefore the peak intensity is lower and more spectral weight remains in the bandlike part. Indeed, the bandlike contribution from this component alone comprises almost 50% of the total bandlike intensity of the M_5VV line. The bandlike part of the other multiplet components makes up the difference. Finally, the $^1S_0$ final state has a relatively high correlation energy with $U/2W\sim 1.3$. The line shape of this two-hole final state before broadening (not shown) consists of a very sharp peak located 2.9 eV below the $^1G_4$ peak and a small bandlike part. When the line profile is convolved with a Gaussian distribution to broaden it out, the Gaussian contribution at 2.9 eV below the $^1G_4$ peak dominates as can be seen in Fig. 4(b). The intensity predicted by the fit in the vicinity of the $^1S_0$ component of the multiplet is somewhat greater than the APECS data in Fig. 5(a). However, the discrepancy might be due to an overestimation of the background around the lower edge of the spectrum at 344 eV. Overall, however, the fitted line follows the APECS data quite closely.

As was the case with the M_5VV data, the fit to the intrinsic line shape of the M_4VV Auger transition, which is presented in Fig. 5(c), closely matches the data between about 351 and 362 eV. In this fit we assume the same values for *U*, the same multiplet splitting and the same amount of Gaussian broadening as were used in fitting the coincidence M_5VV line. In the M_4VV Auger line, the ^3F components of the final-state multiplet are weak relative to the M_5VV transition while the $^1G_4$ and the neighboring $^1D_2$ configurations gain intensity (see Table I). This produces a narrower line than is the case in the M_5VV Auger transitions. Whereas the APECS data show that the M_5VV line is almost 2.8 eV wide (FWHM), the M_4VV transition has a width of only about 1.9 eV. For the bandlike part of the spectrum, the fit again reproduces the data quite well, all the way up to 362 eV where the APECS data approaches a true zero value.

At kinetic energies below the main peak of the M_4VV transition, the $^1S_0$ multiplet component contributes most of the intensity above the background in a peak extending from 348.5 eV to 352 eV. The APECS data show that only a small portion of the intensity in that energy range is unaccounted for by the contribution from the $^1S_0$ final state. This energy range is also where the intensity from an M_4M_5V Coster-Kronig (CK) preceded M_5VV Auger transition should occur. In such a process, an M_4 core electron is photoexcited from the solid. The M_4 vacancy is then filled with an electron from the M_5 level. The M_5 core hole then decays via an M_5VV Auger process. Such a sequence of transitions would result in the ejection from the solid of a $3d_{3/2}$ core electron and a M_5VV Auger electron. As Coster-Kronig transitions are typically much faster than our timing resolution, our APECS apparatus would record this pair of electrons as a coincidence event. However, the overall agreement between the Ag M_4VV APECS data and the model spectrum, particu-

larly near 347.5 eV (the main line of the M_5VV spectrum), shows that the contribution to the Ag M_4VV Auger line from an M_4M_5V CK preceded M_5VV Auger transition is quite small, less than 5%. This observation is in agreement with a photoemission experiment[22] that examined the $3d$ core level line widths of the second row transition metals. In that report,[22] the authors argued that such CK transitions have vanishing strength in $4d$-transition metals for $Z \geqslant 47$ (Ag) since in those metals the spin-orbit splitting of the $3d$ levels is less than the binding energy of the centroid of the valence $4d$ bands.

VI. SUMMARY

We have determined the intrinsic line shapes of the overlapping Ag M_5VV and M_4VV Auger spectra by measuring them in coincidence with $3d_{5/2}$ and $3d_{3/2}$ core photoelectrons, respectively, using high resolution APECS with a synchrotron radiation source. We find that neither bandlike (i.e., a self-convolution of the valence band density of states) nor atomiclike (i.e., an atomic multiplet structure broadened out with Gaussian distributions) line shapes, used separately or in combination, gives a satisfactory account of these Auger spectra. In retrospect, this is not surprising since for Ag $U/2W \sim 1$. As the system is intermediate between the bandlike and atomiclike extremes, it need not be described by some linear combination of those line shapes. Instead, we find that the intrinsic M_5VV and M_4VV line shapes are well described by the CS theory when it is applied separately to each component of the multiplet structure of the $4d^8 5s^2$ Auger final state. Both transition profiles are fit using a correlation energy of 4.8 eV for the $^1G_4$ multiplet with the same energy splittings and relative intensities as were calculated by Parry-Jones, Weightman, and Andrews [7] using a Hartree-Fock approach. These results show that the CS theory gives an excellent account of CVV Auger spectra even in the challenging regime when the Coulomb repulsion energy and the valence band width are comparable.

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