

Complete Screening and Quasiatomic MVV Auger Line Shapes due to Double Core Ionization

A. de Siervo, R. Landers, and G. G. Kleiman*

Instituto de Física “Gleb Wataghin,” Universidade Estadual de Campinas, Caixa Postal 6165, 13081-970 Campinas, SP, Brazil
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MVV spectra of Rh, Pd, and Ag were measured with and without ionization of their L_3 levels. Extra ($MMMVV$) structure corresponds to the $M_{45}M_{45} \rightarrow M_{45}VV$ transition following the $L_3M_{45}M_{45}$ transition. We interpret the $MMMVV$ structure for Pd as quasiatomic in nature from its similarity to the corresponding Ag spectral shape and from its agreement with atomic calculations. The Pd quasiatomic $MMMVV$ spectrum arises from a two final-state hole bound state in the Pd d band filled by screening of the core holes. These findings represent the first unambiguous observation of the influence of complete screening on spectral features.

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Introduction.—Auger electron spectroscopy intrinsically involves only excited states and is a rich probe of many-electron phenomena. One of the most interesting aspects of metallic valence-band Auger spectra involves the connection between screening, correlation of the final-state holes, and the spectral line shape. The observation of the quasiatomic $M_{45}N_{45}N_{45}$ (or MVV) valence-band spectrum of Ag [1] gave rise to the theories of Cini [2] and Sawatzky [3], which provide the conceptual framework within which we interpret these spectra. When the holes' effective Coulomb interaction (U) is much larger than the bandwidth (W), bound states of the two valence-band holes are formed and the MVV spectrum is quasiatomic, as in the case of Ag. When $W \gg U$, the spectrum is bandlike, as for Rh. When $W \approx U$, the spectrum does not present atomic multiplet structure and is strongly influenced by band effects, as in the case of Pd [4,5].

The nature of the valence electron screening of the holes determines the strength of U , or the Lang-Williams Auger parameter [6]. The systematics of Auger parameters from core-hole Auger spectra are explained by models exploiting the complete self-consistent screening of the core holes within the atomic cell [6–10]. According to the excited-atom version of the quasiatomic model (in which core charge is self-consistently transferred to the valence shell to simulate screening) and the equivalent-core approximation (in which valence electrons see the core hole as an additional proton), the d electrons screen the core holes effectively until the d band becomes full, at which point the s electrons, which are more delocalized spatially, assume the role of less effective screening charge [6–8]. Systematic studies [11–13] of the experimental Auger parameters indicate that the screening of d -valence-band holes is strikingly similar to that of core holes, so that the explanation of the strength of U in terms of the nature of the screening electrons appears to be valid for d -valence-band holes as well [4]. The complete screening model is normally assumed to be valid in analyses of spectra such as the MVV spectrum of Pd [4], but direct observation of spectra which are unambiguously associated

with the corresponding fully relaxed states has not been reported.

The Cini-Sawatzky theory [2,3] indicates that the Pd MVV spectrum would become quasiatomic should the Pd d band become full. Indeed, in alloys, quasiatomic Pd MVV spectra have been observed [14], indicating a full Pd d band and a large value of U . Another intriguing possibility arises from the complete screening model: Were we able to create at least two core holes in the initial state of the Pd MVV process, then the complete screening model suggests that screening electrons should fill the Pd d band. Could one expect a truly quasiatomic Auger spectrum? In other words, would the observed spectrum correspond to the transition between the fully relaxed initial and final valence-band states in the presence of the core holes predicted by the complete screening model?

Such a multiple hole Auger initial state would necessarily have to be the final state of some other process. Cascade affected Auger spectra [15–17] have attracted interest from the opportunity of using synchrotron radiation in studies of atoms [18–29] and, to a lesser extent, solids [30–33]. The important point here is that the final MM hole of the LMM transition can serve as the initial state for an MVV transition, such as that which we consider. Since one would like to compare spectra with and without an L hole, it is necessary to utilize synchrotron radiation to ionize the L level.

In this paper, we present results for the x-ray excited Auger (XAES) MVV spectra of Rh, Pd, and Ag measured, with synchrotron radiation excitation, with and without ionization of the respective L_3 levels. The respective spectra change dramatically upon ionization and we attribute the extra structure produced after ionization as corresponding to the $M_{45}M_{45} \rightarrow M_{45}VV$ transition, which is subsequent to the $L_3M_{45}M_{45}$ transition. The extra structure for Pd is markedly similar to that of Ag and different from that of Rh, indicating its quasiatomic nature. Results of atomic calculations for this rather complicated transition agree quantitatively with the experimental spectra of Pd and Ag. These results allow us to interpret the extra spectral structure of Pd as quasiatomic. We attribute the quasiatomic

line shape to a bound state of the two final-state holes in the full Pd d band. We believe the filling of the band to be produced by d -valence electrons, which screen the two initial M_{45} holes. These findings represent the first observation of the clear influence of complete screening on spectral shape.

The decay processes treated here are relevant to theoretical determinations of branching ratios and fluorescent and vacancy yields: these, in their turn, are important for studies of multiple ionization in plasmas and for applications such as in x-ray fluorescent analysis. Our principal results explicitly demonstrate the validity of the complete screening model in the metals treated here, which had been confirmed only indirectly. They suggest complete relaxation of valence-band states of metals for core-level spectroscopies in general and not just for those involving two-hole resonances. The validity of this simple physical model of fully relaxed valence bands in the presence of localized holes should facilitate calculations of spectral line shapes (including Auger decay spectra), as well as spectral energy positions and shifts and contribute to extracting excited-state properties from Auger spectra, in analogy with the use of photoemission for extracting ground-state properties.

Experiment and theory.—The samples were high purity thick foils polished to a mirror finish and then cleaned *in situ* through sputtering (with 2000 eV Ar ions) and annealing cycles until all traces of impurities were removed. The spectroscopic measurements were performed using a bending magnet beam line with the soft x-ray spectroscopy double crystal monochromator ($E/\Delta E = 4000$) at the Brazilian National Synchrotron Laboratory (LNLS) and an Omicron EA 125/HR hemispherical analyzer with multidetection operated in the constant analyzer transmission mode. The overall energy resolution was 1.0 eV.

In order to illustrate the striking nature of the experimental spectra, Fig. 1 presents the MVV spectra of Pd and Ag (L_3 binding energies 3173 and 3351 eV, respectively) in a $Ag_{0.5}Pd_{0.5}$ alloy with photon energies below and above the Pd L_3 threshold but below the Ag L_3 threshold (the nominal photon energies are 3166 and 3174 eV, respectively). In order to correct for any intensity changes, we adjust the Ag M_4VV intensities (at ~ 355 eV) to be the same in the two spectra. There is a very large increase in intensity (by a factor of around 2.1) in the region of the normal Pd MVV (~ 320 – 335 eV) emission upon ionizing the L_3 level as well as the extra structure between the Ag and Pd MVV spectra (~ 335 – 350 eV). The alloy spectrum is well described by a simple combination of the corresponding pure metal spectra. Since the shape of the Pd spectrum in the normal MVV region appears not to change after ionization, it would seem to arise from MVV Auger transitions following contributions from other channels. We attribute the large intensity change to contributions from normal MVV emission, MVV emission following L - M fluorescence, and MVV emission fol-

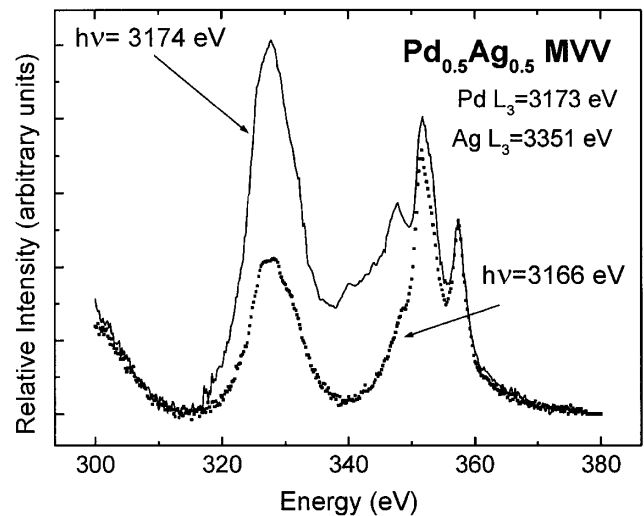


FIG. 1. Experimental MVV spectra of a $Ag_{0.5}Pd_{0.5}$ alloy with (i.e., $h\nu = 3174$ eV) and without (i.e., $h\nu = 3166$ eV) ionization of only the Pd L_3 level.

lowing the Auger cascade process. As we report below, inclusion of these effects, without any adjustable parameters, describes the intensity increase rather well.

In Fig. 2, we present the experimental MVV XAES spectra of Rh (in the inset), pure Pd, and pure Ag with and without ionizing the respective L_3 core level (labeled B and A in the figure, respectively) as functions of energy relative to that of the main (1G_4) peaks; the spectra have been normalized so that the main peaks have the same intensities. The corresponding exciting photon energies are,

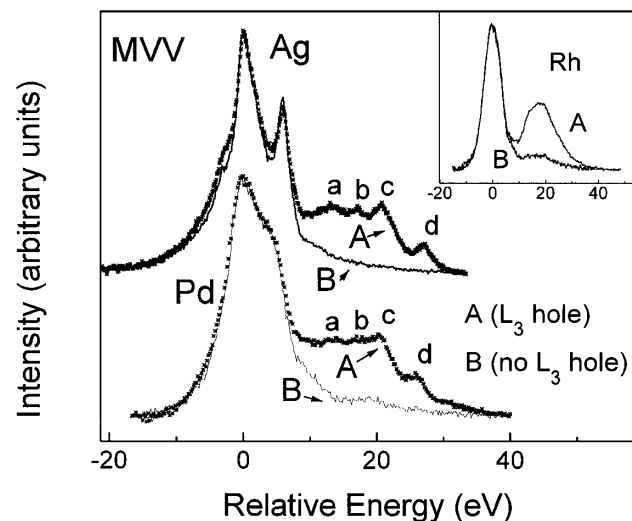


FIG. 2. MVV spectra of Rh, Pd, and Ag with and without ionization of the L_3 level. The energies are relative to those of the main (1G_4) peaks, whose absolute energies are 301.4, 328.0, and 351.7 eV, for Rh, Pd, and Ag, respectively. The spectra with (denoted A in the figure) and without (labeled B) L_3 ionization were, respectively, excited with photon energies of 3006 and 2995 eV for Rh, 3197 and 3164 eV for Pd, and 3364 and 3335 eV for Ag.

respectively, 2995 and 3006 eV for Rh (L_3 binding energy of 3004 eV), 3164 and 3197 eV for Pd, and 3335 and 3364 eV for Ag. The absolute energies of the main peaks are 301.4, 328.0, and 351.7 eV, for Rh, Pd, and Ag, respectively. We have removed the inelastic background [34] from all the spectra in Fig. 2.

Considering first the Rh spectra, we note that the normal MVV spectrum (i.e., without the L_3 ionization) is featureless, reflecting its essentially bandlike nature. Upon ionization, a strong extra structure appears, whose maximum is located at around 20 eV above that of the main peak. From the arguments given above, we associate this extra structure with the transition $M_{45}M_{45} \rightarrow M_{45}VV$ and denote this feature as $MMMVV$. Its featureless nature is expected from the complete screening model. Even in the presence of an extra M_{45} hole, which resembles a core hole to valence electrons, the screening electrons are not sufficient to fill the d band and the effective Coulomb interaction of the two valence-band holes is weak, so that we expect the resulting structure to be bandlike.

The normal MVV regions of the Ag spectra are very similar in both A and B in Fig. 2 and both are strongly quasiatomic in nature. The extra $MMMVV$ contribution after ionization (curve A) has considerable structure and we call attention to the peaks labeled a to d . We attribute the origin of $MMMVV$ to the same transition as in Rh and expect the final-state valence-band holes to be strongly bound in the presence of the extra M_{45} hole. Within this interpretation, the peaks a to d reflect the atomic multiplet structure produced by the coupling of the three final-state holes (M_{45} and two valence-band holes).

The Pd spectra are more interesting. Again the normal MVV regions in Fig. 2 are very similar and are not quasiatomic, which reflects the weakly bound state of the two final-state valence-band holes of the MVV spectra. Examination of the $MMMVV$ region, however, indicates the presence of considerable structure, notably the peaks a to d indicated. The similarity with the Ag $MMMVV$ region is striking. On the basis of this comparison, one would be led to conclude that the Pd $MMMVV$ structure is truly quasiatomic in nature, indicating a strongly bound state of the two final-state valence-band holes. Such a strongly bound state would seem possible only if the d band were full. That is to say, the shape of the structure presented seems possible only because the screening electrons have filled the Pd d band.

We also performed calculations from nonrelativistic atomic theory [35–38] of the probabilities of the $M_{45} \rightarrow M_{45}VV$ and $M_{45}M_{45} \rightarrow M_{45}VV$ transitions. Details of the calculation are complicated and we reserve them for discussion elsewhere [39]. Theoretical results for Pd are presented in Fig. 3 along with the same Pd experimental spectra as in Fig. 2. We display the envelopes of both the total theoretical spectrum, spectrum (c) in the figure, and the $MMMVV$ contribution, (d). The normal MVV spectrum was calculated within the jj -intermediate

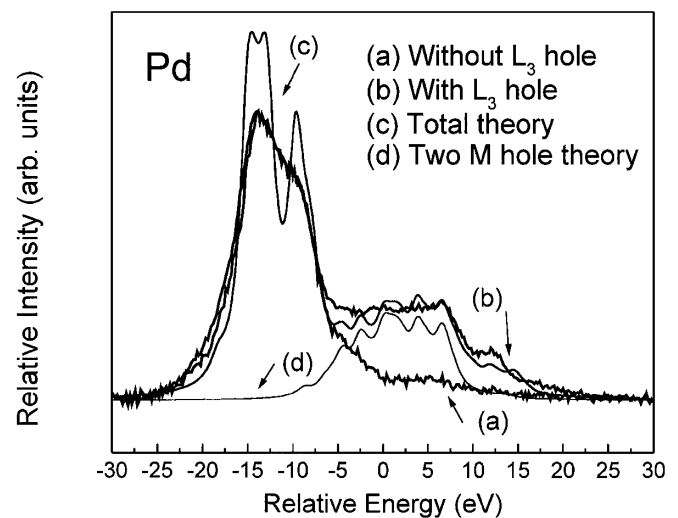


FIG. 3. Comparison of the Pd spectra of Fig. 2 with the results of atomic calculations. The total theoretical envelope and the experimental $MMMVV$ spectrum are normalized to coincide at peak c of Fig. 2.

coupling scheme [40], whereas the jj -LS scheme [40] seemed necessary to describe the $MMMVV$ shape. We formed the envelopes by convoluting a Voigt function of half-width 2.0 eV with the appropriate multiplet term. The theoretical and experimental spectra were made normalized so that they coincided at peak c in Fig. 2.

We should mention that we formed the total theoretical spectrum by combining fluorescence [41–43], normal Auger, satellite contributions, and Auger cascade processes. The parameters used were either experimental or calculational [39], and, except for the Voigt function widths, there were no adjustable parameters.

We call attention to three of the features of Fig. 3. First, the atomic calculations are reasonably successful in describing the $MMMVV$ spectrum of Pd but fail to agree with the MVV spectrum, which is modified by band effects. Another point is that the peaks a – d in Fig. 2 all have their theoretical counterparts in Fig. 3, supporting our quasiatomic interpretation. Finally, we observe that the relative intensities of the theoretical and experimental spectra are very similar, especially considering that there were no adjustable parameters in the calculation. Similar agreement is reached for Ag.

Conclusions.— Ionization of the L_3 level produces sizable extra structure in the MVV spectra of Rh, Pd, and Ag. The extra structure is associated with the transition from the $M_{45}M_{45}$ two-hole state (which is the final state of the $L_3M_{45}M_{45}$ Auger transition) to the $M_{45}VV$ three-hole state, denoted as the $MMMVV$ transition. The shapes of the $MMMVV$ and MVV transitions of Rh and Ag upon L_3 level ionization are very different from each other and are in agreement with the complete screening model. Those of Rh are bandlike, while those of Ag are quasiatomic. Pd, on the other hand, presents a different behavior. The MVV spectra with and without L_3 level ionization have the

same shape, which is associated with final-state valence-band holes which are only weakly bound, so that the *MVV* spectra have strong band effects. The *MMMVV* spectrum of Pd, however, is very similar in shape to that of Ag, indicating its quasiautomic nature. The results of atomic calculations agree reasonably well with the experimental Pd *MMMVV* spectrum, in shape as well as in relative intensity. The calculations cannot describe the shape of the *MVV* spectrum. We conclude that the Pd *MMMVV* spectrum is truly quasiautomic in nature. Our conclusion is in contrast to the situation in alloys where quasiautomic Pd valence-band spectra have been observed [14]. The alloy result is consistent with filling of the Pd *d* band in the initial state of the transition as a consequence of alloying. Within the context of the Cini-Sawatzky theory [2,3] and the complete screening model [6–10], the quasiautomic Pd *MMMVV* must be associated with a full initial-state *d* band, which is filled by *d*-screening electrons. In short, the *MMMVV* transition can be considered as occurring between the fully relaxed initial state of the system with two M_{45} holes and the fully relaxed final state with one M_{45} and two valence-band holes. In other words, this paper reports the first observation of unambiguous quasiautomic spectral structure produced purely by screening mechanisms.

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*Corresponding author.

Electronic address: kleiman@ifi.unicamp.br

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