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Deviations from one-electron behavior in the Ag and Pd $M_{4,5}$-VV Auger spectra of Ag_cPd_{1-c} alloys

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A systematic investigation of the Ag and Pd $M_{4,5}$-VV Auger spectra in the pure metals and in the Ag_cPd_{1-c} $(0.1 \leq c \leq 0.9)$ alloys is presented. The shape of the Auger spectra is discussed in relation to the values of the effective Coulomb interaction U_{eff} between the two holes present in the final state of the Auger transition and of the width W of the one-electron local densities of states as obtained from $L\beta_{2,15}$ soft-x-ray emission bands. The Auger spectra of Ag in the metal and the alloys have a pronounced quasiatomic character, as can be expected from the $U_{\text{eff}}/2W$ ratio which is found to be close to unity. The Auger spectrum of pure Pd $(U_{\text{eff}}/2W \approx 0.4)$ can be explained in terms of an atomic model in which strong band effects are present. For alloys with low-Pd content where Pd forms an impurity state, it is shown that final states other than the localized $[4d^2]$ two-hole state have to be invoked to explain the line shape.

I. INTRODUCTION

Much detailed information has become available over the past few years on the density of states of random substitutional alloys. Following photoemission measurements,[1-3] a confrontation between theoretical calculations and soft-x-ray spectroscopy (SXS) measurements on Cu_cNi_{1-c} and Ag_cPd_{1-c} have clearly shown that they form a split-band system at all concentrations.[4,5] Because of the strongly localized character of the core wave functions, SXS has the particular advantage of being a probe of the local density of states (LDOS). From x-ray photoelectron spectroscopy (XPS) determinations of the appropriate core-level binding energies, it is possible to situate the LDOS precisely with respect to the Fermi level.

Auger-electron spectroscopy measurements of core-valence-valence transitions (denoted hereafter as X-VV) are an alternative way of obtaining information on the LDOS in alloys as the intra-atomic part of the Auger decay rate is much larger than the interatomic part.[6] An interpretation of such processes, however, is less straightforward since Auger transitions involve a final state with two holes in the valence band. The kinetic energy of an X-VV Auger electron may be written as the difference between the binding energies in the initial one-hole and final two-hole states

$$E(X-V_1V_2)=E(X)-E(V_1V_2). \tag{1}$$

By introducing the effective Coulomb interaction $U_{\text{eff}}(V_1V_2)$ of the holes present in the final state, use can be made of the one-electron binding energies $E(X)$, $E(V_1)$, and $E(V_2)$ by means of the relation

$$E(X-V_1V_2)=E(X)-E(V_1)-E(V_2)-U_{\text{eff}}(V_1V_2). \tag{2}$$

Recent experimental and theoretical work has shown that two limiting cases may be considered in treating the X-VV Auger spectra from metals with initially filled narrow bands (see Refs. 7–10 for a discussion and further references). If the one-electron bandwidth W is such that $U_{\text{eff}}/2W << 1$, the shape of the X-VV Auger spectrum is given by the self-convolution of the one-electron density of states weighted to account for the transition matrix elements as originally proposed by Lander.[11] However, if $U_{\text{eff}}/2W >> 1$, the X-VV Auger spectrum is almost entirely constituted of atomiclike features, i.e., it reflects a local two-hole density of states. This is due to the fact that, since the repulsive energy between the two holes in the final state is larger than the bandwidth, none of the holes can be filled by a band electron for energy conservation reasons.

To date only one experiment involving a continuous variation of the $U_{\text{eff}}/2W$ ratio has been performed. It concerns the Ag $M_{4,5}$-VV Auger spectra in silver-simple metal alloys.[12] The only calculation on the evolution of the shape of X-VV transitions as a function of the $U_{\text{eff}}/2W$ ratio available has dealt with a simple cubic tight-binding s band.[13] Thus, although some progress has been made in the understanding of X-VV Auger transitions, it is of interest to obtain further experimental data, in particular for alloys involving two d-band metals.

In view of the data available from SXS-XPS experiments concerning the changes in LDOS widths as a function of composition in Ag_cPd_{1-c}, we have recorded the Ag and Pd $M_{4,5}$-VV Auger spectra over the range $0.1 \leqslant c \leqslant 0.9$ with the purpose of investigating the effect of the one-electron density of states on the Auger line shape and discussing the results in relation to the models at present available for such Auger processes.

After a brief description of the experimental techniques employed (Sec. II), the SXS measurements of the LDOS are reported (Sec. III A). The $M_{4,5}$-VV Auger spectra are given and their evolution discussed, when the alloy composition is varied, in Secs. III B and III C for Ag and Pd, respectively. Conclusions are drawn in Sec. IV.

II. EXPERIMENTAL PROCEDURE

The alloys were prepared by melting under an argon atmosphere appropriate amounts of high purity (99.99%) Ag and Pd cut from rods. The pellets so obtained were cold rolled into 0.2-mm thick strips, parts of which were used for both SXS and XPS-Auger studies. An analysis of the intensities of the core-level peaks of each constituent reveals that the surface composition of our samples was systematically 20% richer in Ag than expected. Such an enrichment has also been noted by Hüfner *et al.*[2] The x-ray emission measurements involve a much greater sample thickness (≈ 1000 Å) than the XPS-Auger experiments and are therefore expected to correspond to samples with bulk compositions. We consider that the differences in effective composition are small enough to be neglected and the nominal values are used hereafter. The SXS emissions were induced by 6.5-keV electrons and analyzed with a 0.5-m radius bent quartz $(10\bar{1}1)$ crystal at a resolution setting $(\Delta E/E)$ of 2×10^{-4}. The mounting has been described in detail elsewhere.[14]

The XPS and Auger measurements were performed by means of an electrostatic hemispherical analyzer operated under a relative energy resolution of 7×10^{-4}.[15] The x rays emitted from an Al anode excited by 12-keV electrons were used to produce the electron spectra. After Ar^+ ion etching at low doses to avoid segregation at the surface of the alloys,[16] almost all traces of carbon and oxygen contamination disappeared.

The residual gas pressure was of the order of 10^{-5} Pa for the SXS experiments and 10^{-7} Pa for the XPS-Auger determinations.

III. RESULTS AND DISCUSSION

A. 4d local densities of states

The Ag and Pd LDOS were investigated by means of the $L\beta_{2,15}(4d \rightarrow 2p_{3/2})$ SXS emission bands. Although the $5s \rightarrow 2p_{3/2}$ transition is allowed by dipole selection rules, the $5s$ contribution to the spectrum is negligible. The emission bands thus reflect the $4d$ distributions. A detailed description of the variation of the $4d$ LDOS as a function of compositon will be given elsewhere along with the emission bands calculated in the Korringa-Kohn-Rostoker coherent-potential approximation (KKR-CPA).[5] Here we only mention the features which are relevant to a discussion of the X-VV Auger spectra, namely the energy positions of the LDOS peaks relative to the Fermi level and the LDOS widths.

The most precise way of locating the individual $4d$ LDOS obtained by SXS with respect to the Fermi level is from core-level binding-energy measurements performed on the same samples. The energy of the Al $K\alpha$ line used to induce the XPS spectra being insufficient to ionize the tightly bound $2p_{3/2}$ levels, the $3d_{5/2}$ binding energies in the alloys were measured. The $2p_{3/2}$ binding energies are then deduced by adding the $L\alpha_1$ $(3d_{5/2} \rightarrow 2p_{3/2})$ x-ray transition energy. This is a standard procedure used to obtain binding energies for levels beyond the scope of XPS measurements with Al $K\alpha$.[17] The validity of this procedure is verified when the experimental $L\alpha_1$ x-ray transition energies are compared to the differences between the $3d_{5/2}$ and $2p_{3/2}$ XPS binding energies in systems where both sets of data are available: x-ray transition energies agree with differences in XPS binding energy to better than 0.2 eV, i.e., to within the experimental precision.[18] The SXS and XPS measurements on the alloys were all calibrated with respect to the pure elements so that the relative positions of the LDOS from sample to sample is known to ±0.05 eV.

In Fig. 1, we present the $L\beta_{2,15}$ emission bands for the pure elements, for Ag in $Ag_{0.10}Pd_{0.90}$ and for Pd in $Ag_{0.90}Pd_{0.10}$ situated relative to the Fermi level as described. The peak positions of the Ag and Pd $4d$ LDOS are given in Table I along with their full width at half maximum (FWHM). It is seen that upon alloying the Ag $4d$ LDOS shifts towards the Fermi level and broadens with increasing Pd content. The Pd LDOS shifts also towards the Fermi level but narrows as the Ag content increases.

The narrowing of the Pd band is well accounted for by the KKR-CPA calculations which show that as the Pd content diminishes the Pd states form an impurity band.[19] Such a behavior was also noted for Ni in Cu_cNi_{1-c}.[4] However in the latter example no change in bandwidth was predicted nor observed for the Cu LDOS and similarly no theoretical justification has been found for the Ag states. In fact the calculations predict a slight narrowing of the Ag band as the Ag content diminishes, which is more in accordance with the Ag distributions unfolded from the XPS total densities of states[2] and ultraviolet photoemission measurements.[3] This discrepancy has not yet been

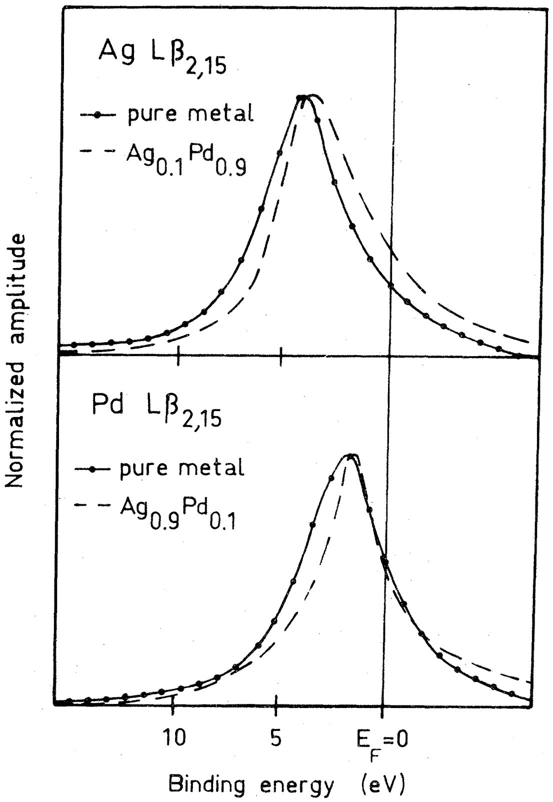

FIG. 1. $L\beta_{2,15}$ x-ray emission bands of Ag in the pure metal and $Ag_{0.10}Pd_{0.90}$, and Pd in the pure metal and $Ag_{0.90}Pd_{0.10}$.

explained. It should be emphasized that such a broadening of the Ag x-ray emissions has also been reported by other authors.[20]

Corrections have to be made to the measured emission bandwidths, however, as an estimation of the true bandwidths will also be required. Optimum resolution conditions for the SXS measurements could not be used because of the low intensities encountered at the extreme compositions and in any case the emissions are also subject to appreciable broadening due to the $2p_{3/2}$ inner-level width. As the instrumental broadening is 0.6 eV (see Sec. II) and $2p_{3/2}$ inner-level width is 1.9 eV,[21] we estimate the total experimental broadening to be 2.5 eV,[21] we estimate the total experimental broadening to be 2.5 eV. A Gaussian-type correction has been applied to obtain the true LDOS widths except for the narrow Pd band in $Ag_{0.90}Pd_{0.10}$. In the latter case the recorded LDOS width is almost equal to the broadening effects so a linear correction is more appropriate as a Gaussian correction would lead to an underestimate (see Table I).

B. Ag $M_{4,5}$-VV Auger spectra

The $M_{4,5}$-VV Auger spectra of Ag in the pure metal and the $Ag_{0.10}Pd_{0.90}$ alloy are given in Fig. 2. The spectra have been normalized to the same amplitude after subtracting the background and the contribution from inelastic scattering. The transmission of the electron analyzer has been assumed to be constant over the narrow energy range studied. The two main components observed in the curves are attributed to the M_5-VV and M_4-VV spectra. They lie 6.0 eV apart, which is equal to the M_4-M_5 spin-orbit splitting in Ag as measured by XPS.

Fine structure is clearly resolved in the spectrum of pure Ag, and the M_5-VV and M_4-VV components have different shapes. Also the spectrum resembles the Xe $M_{4,5}$-$N_{4,5}N_{4,5}$ Auger spectrum (see for instance Ref. 22), so it may be assumed to have a marked atomic character. In Fig. 2 the spectrum is compared to a model calculation performed in the atomic limit. A detailed description of the calculation has been given elsewhere,[23] but a brief summary of the method employed follows as it has also been applied to Pd (see Sec. III C).

The role played by the 5s electrons present in the Ag valence band was supposed to be negligible.

TABLE I. Energy positions relative to the Fermi level and FWHM of the Ag and Pd 4d LDOS in the pure metals and some Ag_cPd_{1-c} alloys as obtained from combined SXS-XPS measurements. All values are in eV.

Sample	E_{4d}^{Ag}	E_{4d}^{Pd}	$W_{expt.}^{Ag}$	$W_{corr.}^{Ag}$	$W_{expt.}^{Pd}$	$W_{corr.}^{Pd}$
Ag	4.7	···	4.5	3.7	···	···
$Ag_{0.90}Pd_{0.10}$	4.7	1.8	4.7	4.0	3.5	1.0
$Ag_{0.10}Pd_{0.90}$	4.1_5	2.1	5.3	4.2	4.7	4.0
Pd	···	2.1	···	···	4.9	4.2

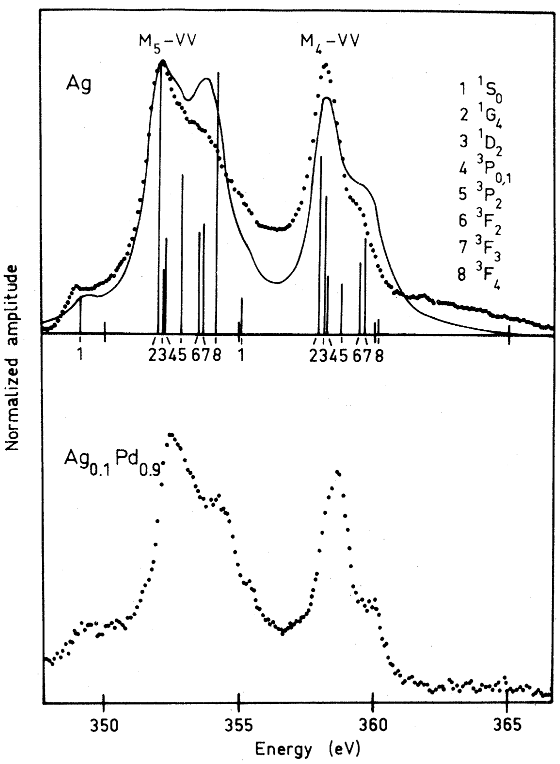

FIG. 2. Ag $M_{4,5}$-VV Auger spectrum in the pure metal (compared to the spectrum calculated in the atomic limit) and in $Ag_{0.10}Pd_{0.90}$.

Their contribution to the Auger spectrum was therefore ignored, i.e., a $4d^8$ final-state configuration was chosen for the Auger process. The final-state levels were calculated in intermediate coupling. The Slater-Condon integrals F^k were taken from a Hartree-Fock calculation[24] and reduced by 20%. This reduction was necessary to account for the observed level splitting as a nonrelativistic procedure was used. The spin-orbit parameter ζ_{4d} was deduced from optical data.[25] The intensities were obtained by treating the initial state of the Auger process in *jj* coupling and the final state in intermediate coupling. Once the transition amplitudes were obtained in the mixed coupling scheme,[26] the transition rates were deduced using the components of the energy-matrix eigenvectors and the radial matrix elements computed from Herman-Skillman wave functions.[27] Each line predicted in this way was then replaced by a Lorentzian profile to simulate the experimental spectrum. The best fit, visually, was obtained for a profile of 1.25 eV FWHM. This value is much lower than the one-electron Ag bandwidth (3.7 eV). On comparing the experimental and simulated spectra (Fig. 2), it is seen that the fine structure observed can be explained almost entirely by the existence of an Auger final state with two bound holes in the valence band. This is compatible with the fact that the U_{eff} value for the prominent M_5-$VV(^1G_4)$ line, as determined from combined SXS, XPS, and Auger energy measurements using Eq. (2), leads to a $U_{\text{eff}}/2W$ ratio equal to unity (see Table II). It is an indication of atomiclike behavior.

Two discrepancies only are apparent between the model and experimental spectra: the atomic calculation overestimates the intensities of the ^3F lines and it does not predict the existence of the low intensity and broad feature in the 360–365-eV region. An explanation for this can be found if one considers that the average U_{eff} value for the ^3F components is lower than the U_{eff} value for the $^1G_4$ component (see Table II). According to the $U_{\text{eff}}/2W$ criterion, this is an indication that the ^3F lines might lose in part their quasi-atomic character, the $^1G_4$ line remaining unaffected. Indeed it is found that the delocalized $[4d,4d]$ hole-state, which can be constructed from the self-convolution of the one-electron LDOS as given by SXS, overlaps the $[4d^2;^3F]$ states but not the $[4d^2;^1G_4]$ state. Thus the $[4d^2;^3F]$ states have a shorter lifetime than the $[4d^2;^1G_4]$ state and so appear to be less intense than predicted on the basis of

TABLE II. Binding energies and Auger energies for Ag in the pure metal and in the $Ag_{0.10}Pd_{0.90}$ alloy (all values in eV) together with the corresponding $U_{\text{eff}}/2W$ ratios.

Sample	Line	$E(M_5-VV)$	$E(M_5)$	$E(V)$	U_{eff}	W	$U_{\text{eff}}/2W$
Ag	$^1G_4$	351.9	368.1	4.7	6.8	3.7	0.92
	$^3F_{2,3,4}$	353.4			5.3		0.72
$Ag_{0.10}Pd_{0.90}$	$^1G_4$	352.3	367.8	4.1_5	7.2	4.2	0.86
	$^3F_{2,3,4}$	353.8			5.7		0.68

an atomic model alone. Then, part of the Auger intensity will also be transferred to the region corresponding to the $[4d,4d]$ distribution, i.e., at a higher kinetic energy than the atomic spectrum. Confirmation has been obtained from recent experimental observations of the Ag $M_{4,5}$-VV spectra in the Ag_3Mg_{97} alloy[12] and in ultra-thin-Ag films[28] where the Ag valence band is so narrow that any overlap between the delocalized $[4d,4d]$ and the localized $[4d^2]$ distributions is absent, and where there is then excellent agreement with the atomic model.

The Ag $M_{4,5}$-VV Auger spectrum in the $Ag_{0.10}Pd_{0.90}$ alloy (Fig. 2) is very similar to the pure-metal spectrum. As expected from the arguments set out in Sec. III A concerning the Ag bandwidth, the change in $U_{eff}/2W$ is not sufficiently significant to modify the overlap between the $[4d,4d]$ and the $[4d^2]$ states.

C. Pd $M_{4,5}$-VV Auger spectra

The $M_{4,5}$-VV Auger spectrum from pure Pd is given in Fig. 3. The M_5-VV and M_4-VV components separated by 5.3 eV are resolved as in the Ag spectrum but here no fine structure is apparent. A value of 4.3 eV is deduced for U_{eff} from the location of the maximum of the M_5-VV component and the $U_{eff}/2W$ ratio is found to be of the order of 0.4 (Table III). This indicates that a bandlike behavior should be present if not dominant. So we have constructed an Auger spectrum model from two self-convoluted bands taken in the ratio 3/2 and separated by 5.3 eV to account for the spin-orbit splitting. The SXS valence band was used for this self-convolution. The model and experimental spectra are compared in Fig. 3. There is general agreement in shape but the band model lies at a kinetic energy about 3 eV too high compared to the experiment. The difference is too large to be attributed to a matrix element effect or to the use of the SXS band in the self-folding procedure. It is more likely to be due to the fact that no correlation between the holes is included in the model as should be required when the value of U_{eff} is only a little smaller than $2W$.

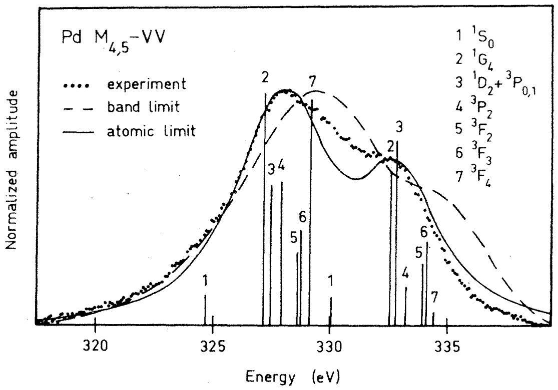

FIG. 3. Pd $M_{4,5}$-VV Auger spectrum in the pure metal compared to the spectra calculated in the atomic and the band limit.

A calculation in the atomic limit has also been performed according to the procedure followed for Ag and described in Sec. III B. The initial-state configuration of Pd is assumed to be $4d^{10}$ though it should be noted that de Haas–van Alphen measurements on pure Pd indicate that the $4d$ band contains 9.6 electrons.[29] A reasonably good fit between the atomiclike model and the experiment can be obtained using a 3.5-eV FWHM Lorentzian profile for each theoretical line and a U_{eff} value of 3 eV (Fig. 3). Such a large broadening is consistent with the overlap between the $[4d^2]$ and $[4d,4d]$ states. It is also met with in the L_3-VV Auger spectrum of Ni.[30–32] This spectrum exhibits fine structure similar to that observed in the atomiclike L_3-VV Cu spectrum but due to the reduced value of U_{eff} (≈ 8.0 eV in Cu and ≈ 4.5 eV in Ni) the Ni lines are ≈ 1 eV broader than the Cu lines. However, it must be recalled that the atomic model overestimates the intensity of the ^3F lines relative to the $^1G_4$ line. This seems in contradiction with the fact that the atomic-model spectrum is less intense than the observed spectrum in the region of the ^3F lines.

TABLE III. Binding energies and Auger energies for Pd in the pure metal and in the $Ag_{0.90}Pd_{0.10}$ alloy (all values in eV) together with the corresponding $U_{eff}/2W$ ratios.

Sample	Line	$E(M_5-VV)$	$E(M_5)$	$E(V)$	U_{eff}	W	$U_{eff}/2W$
Pd	Max.	327.9	335.3	2.1	3.2	4.2	0.38
$Ag_{0.90}Pd_{0.10}$	A	327.3	335.0	1.8	4.1	1.0	2.05
	B	330.1			1.3	···	···

Some elucidation of the origin of the line shape may be expected from the behavior of the Pd $M_{4,5}$-

VV Auger spectra in Ag_cPd_{1-c} alloys. Indeed we have shown in Sec. III A that the Pd $4d$ band narrows to an impurity state and shifts closer to the Fermi level upon alloying with increasing amounts of Ag. Thus the Pd Auger spectrum could be expected to become atomiclike in Ag-Pd alloys with low-Pd content. What happens in fact (Fig. 4) is that the two main components seen in the pure-metal spectrum are still present in the alloy and lie at a slightly lower energy (these components are labeled A and C in the $Ag_{0.90}Pd_{0.10}$ spectrum of Fig. 4). Moreover two features (labeled B and D) develop; they are situated some 3 eV above A and C, and are therefore approximately separated by the Pd $3d$ spin-orbit splitting.

Limiting the discussion to the distinctly more intense M_5 part of the spectrum in $Ag_{0.90}Pd_{0.10}$, one notes that the U_{eff} value for peak A is 4.1 eV, leading to $U_{\text{eff}}/2W \approx 2$ (see Table III). This peak may be attributed to the atomiclike Auger spectrum involving the localized $[4d^2]$ final states. Despite the large value of the $U_{\text{eff}}/2W$ ratio and hence the nonoverlapping of the $[4d^2]$ and $[4d,4d]$ states, no fine structure seems to be resolved in the spectrum, contrary to what occurs in pure Ag with $U_{\text{eff}}/2W \approx 1$. It has been predicted however that in the case of an incompletely filled band, and the Pd impurity state falls into this category, that the X-VV Auger spectrum will broaden due to the possible decay of the $[V^2]$ states on the creation of electron-hole pairs.[33] For peak B, the U_{eff} value drops to about 1 eV and a bandlike origin may be sought for. As the two $4d$ holes in the valence band remain localized and give rise to the $[4d^2]$ atomiclike peak A, a $[4d,5s]$ final state may be considered. In Cu, the M_1-VV Auger spectrum has been observed to involve both $[3d^2]$ and $[3d,4s]$ final states.[34] Nevertheless it must be noted that the $(M_1{-}3d4s/M_1{-}3d3d)$ intensity ratio is close to 1 in Cu, whereas the $(M_{4,5}{-}4d5s/M_{4,5}{-}4d4d)$ intenstity ratio is expected to be much smaller (≈ 0.02) for Pd.[27] The convolution of the narrow $4d$ band with the $5s$ LDOS is certainly expected to lead to a sharp feature as the s states are themselves pushed down into a narrow band due to an antiresonance effect with the d states, particularly at the impurity limit.[35] Thus although the intensity of the sd process is low, the amplitude of the resulting convoluted band could be appreciable.

In the absence of a satisfactory theoretical treatment of these Auger processes, it is suggested that such an interpretation provides a reasonable explanation of the unusual structure apparent in the Pd $M_{4,5}$-VV Auger spectra of Ag_cPd_{1-c} alloys with low-Pd content. It could also account for the discrepancy between the observed pure-Pd spectrum and the atomic model. Here the convolution of a $5s$ peak with the broad $4d$ LDOS would lead to a broad feature of weak amplitude and would not be expected to be resolved.

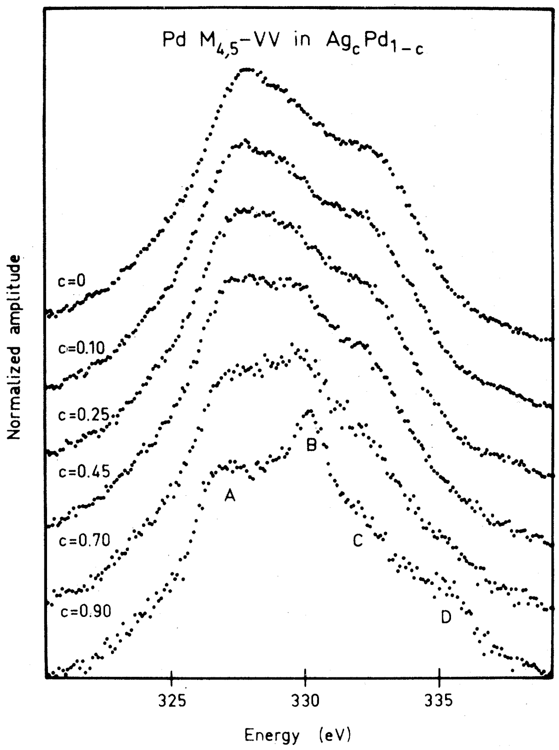

FIG. 4. Pd $M_{4,5}$-VV Auger spectra in the pure metal and Ag_cPd_{1-c} alloys ($0.10 \leq c \leq 0.90$).

IV. CONCLUSION

The Ag and Pd $M_{4,5}$-VV Auger spectra in the pure metals and Ag_cPd_{1-c} alloys depart strongly from those expected when independent-electron behavior is assumed. For pure Ag, a marked atomic character is observed and the departure from a pure atomic calculation is shown to be due to a partial overlap of the localized $[4d^2]$ and delocalized $[4d,4d]$ hole states. This interpretation is supported by the analysis of the $Ag_{0.10}Pd_{0.90}$ spectrum using Ag $4d$ LDOS given by SXS. In the case of Pd a similar situation occurs with a further complication arising from the partially filled nature of the Pd $4d$ LDOS which develops into an impurity state as the Ag content increases. It would also seem that the presence of $4d$ holes alone cannot explain entirely the Pd spectrum.

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