Strong evolution of the p-projected empty density of states in Pd-Al alloys: An $M_{4,5}$ x-ray-absorption-spectroscopy investigation

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We present a near-edge x-ray-absorption investigation on the Pd $M_{4,5}$ edge of Pd, $Pd_{0.85}Al_{0.15}$, PdAl, and $PdAl_3$, and on the Ag $M_{4,5}$ edge of Ag. A comparison with theoretical results for the pure elements Pd and Ag indicates this kind of spectroscopy to be related to the p-projected density of states above the Fermi level via a $3d \rightarrow 5p$ dipole allowed excitation. A direct estimation of the Ag $M_{4,5}$ core-hole lifetime width value (0.4±0.05 eV) is furthermore accomplished. The dramatic changes of the investigated line shapes on going from pure Pd to an increasing dilution of Pd atoms into an Al matrix host suggest a strong participation of the p states to the formation of the chemical bonding which has been undervalued up to now.

INTRODUCTION

In recent years much effort has been devoted to the study of the electronic structure of transition metals and their alloys, especially in connection with the modification of the chemical bonding due to the presence of different atomic species. These studies are of interest for technological and more fundamental areas of research. From the point of view of applied physics, themes such as catalysis and mechanical properties (e.g., hardness, weight, anticorrosion) make alloys particularly interesting. On the other hand, the possibility of exploiting alloys in order to isolate or create physical phenomena that do not exist in elemental materials or that are suppressed by other stronger effects (e.g., the Kondo effect, the virtual bound state in alloys with magnetic impurities) provides an important opportunity to obtain a deeper understanding of the electronic structure of matter.

Recently, many theoretical and experimental studies have provided a large body of information regarding alloying effects: a wide variety of experimental spectroscopies [e.g., x-ray absorption spectroscopy (XAS) x-ray photoemission spectroscopy (XAS), x-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS), x-ray emission spectroscopy (XES), bremsstrahlung isochromat spectroscopy (BIS), and Auger electron spectroscopy and theoretical models have been implemented in order to obtain a better understand-

ing of the electronic properties of such alloys.[1]

In the case of quasinoble metals, in particular Pd and Ni, Fuggle and co-workers[2-4] performed a systematic valence-band and core-level XPS, Auger, and theoretical study on alloying effects with many different partners. In the case of simple metal partners, such as Al and Mg, their major conclusion was that a strong Pd (Ni) d-Al (Mg) p hybridization takes place in all the different alloy concentrations. This interpretation has been confirmed by theoretical[5] and experimental BIS, XES, and XAS results[6-8] and extended to the empty density of states (DOS) energy region, thus giving a well-defined view of the bonding mechanisms acting in these systems. Because of a large absorption cross section of d electrons, the Pd d-derived signal is overwhelming compared with the other orbital components for both x-ray and UV energy ranges. This fact has biased theoretical investigations toward limiting their interest to the Pd (Ni) d and Al p states, leaving totally unexplored the involvement and the role of Pd p and s states in the alloy formation.

In this work, we report the first systematic study of the Pd p-derived DOS above the Fermi level (E_F) in the Pd-Al system with different concentrations: pure Pd, $Pd_{0.85}Al_{0.15}$, PdAl, and $PdAl_3$. These results have been achieved by near-edge excitation of the Pd $M_{4,5}$ edge. For a given initial state (d in this case) dipole selection rules select the angular momentum of the final states as $\Delta l = \pm 1$ (i.e., p and f symmetry for the minus and the plus signs, respectively). Despite the much larger [about

100 times (Ref. 9)] matrix element for $d \rightarrow f$ than for $d \rightarrow p$ transitions, the near-edge part of the spectra are related to the one-particle p-derived empty DOS as recently shown by Paolucci *et al.*[10] in the case of Pd. In fact, due to the difficulty the $4f$ wave function has in penetrating the centrifugal potential $l(l+1)/mr^2$ in order to overlap the $3d$ core, there is a delayed nature to the $M_{4,5}$ edges as far as the $3d \rightarrow 4f$ excitation is concerned, which, in the case of Pd and Ag, start at about 30–40 eV above the threshold energy.[10,11] On the other hand, it is worth noting that the information contained in the near-edge $M_{4,5}$ line shapes cannot be extracted by K or L_1 XAS excitation edges (via the $1s \rightarrow 5p$ or $2s \rightarrow 5p$ absorption channel respectively) because of the much higher lifetime broadenings of these holes [≈ 5–6 eV (Ref. 12)] compared to the $M_{4,5}$ holes [≈ 0.4 (Ref. 13)], which totally wash out the fine structure of the measured line shapes. After showing a comparison between our results and the calculated p state above E_F for pure Pd and Ag (which provides a useful guideline for understanding the alloy line shapes and gives a direct and precise estimation of the typical lifetime broadenings related to the $M_{4,5}$ edges), we will show how a small concentration of Al atoms dramatically changes the distribution of the empty p states and the further modifications related to an increasing Pd-Al coordination. The strong similarity between the $PdAl_3$ and the Ag profiles is exploited to suggest a Pd p-d interaction. Possible Pd $5p$-Al $3p$ coupling is furthermore considered in relation to recent results in literature.

EXPERIMENTAL

Alloy preparation has been performed by melting high-purity Pd and Al together under argon in an arc furnace. For the different stoichiometries, the proper weights of material have been used. No loss of weight occurred during melting. The sample compositions were finally checked with x-ray powder diffractometry. The intermetallics PdAl and $PdAl_3$, and the $Pd_{0.85}Al_{0.15}$ system were found. High-purity Pd (99.95%) and Ag (99.999%) polycrystalline bulk samples have been obtained from rods.

All the measurements have been carried out at the High Energy Spherical Grating Monochromator beam line at the Synchrotron Radiation Source at Daresbury (U.K.).[14] The beam line is based on a spherical grating monochromator (SGM) without entrance slit, that covers the whole photon energy range 250–1400 eV, employing three interchangeable gratings of line spacing 1050, 1500, and 1800 lines/mm. The reported data have been collected using the first grating. In the photon energy range of interest for the Pd and Ag $M_{4,5}$ edges (about 300–400 eV), the full-width–half-maximum (FWHM) resolution was about 0.4 eV. The base pressure during measurements was in the low 10^{-10}-mbar range. All the samples were cleaned *in situ* by a soft Ar sputtering procedure ($p = 1 \times 10^{-5}$ mbar). The signal was collected in the total-yield mode, thus ensuring a high bulk sensitivity to the measurements. This was confirmed by the very small effect induced by the sputtering. In fact, for each sample,

the atomic jumps, measured as the ratio of the signal intensity well above (≈ 100 eV) the Pd and Ag $M_{4,5}$ edges to the signal intensity just below the edges, do not show any appreciable change before and after the cleaning procedure. Furthermore the variations of the atomic jump values in the different alloys, as compared to the pure Pd, show a scaling proportional to the content of Pd atoms as determined by the nominal concentrations and the crystalline structures. This evidence rules out any possibility of strong effects due to preferential sputtering at the surface as far as the surface sensitivity of the experimental probe is concerned. The signal has been normalized to the incident flux collected on line from both a periodically sputtered Ta mesh and a Cu thick film freshly evaporated onto a similar mesh. Very similar results have been obtained for the two cases in the near-edge energy region. All the reported data refer to the Ta normalized spectra. Cleanliness of samples was checked before and after each measurement by XAS at the O and C,K edges. For all the spectra shown, the signal intensity from both O and C was below the instrumentation sensitivity.

RESULTS AND DISCUSSION

In the case of Ag and Pd, the calculated p-projected DOS's are available in literature.[15–17] In Fig. 1(a) the computed profiles are displayed above E_F. The remarkable agreement between these different calculations, apart from minor discrepancies in the case of Ag for energies higher than ≈ 4 eV, makes us confident about the DOS's reliability. In order to make a comparison between our experimental results and the theoretical calculations, we must take into account all the different experimental broadening sources, namely the Gaussian contribution ($FWHM_g$) due to the experimental resolution, and the Lorentzian broadening intrinsically related to the final-state lifetime of the excitation process. This last term is the sum of a constant with $(FWHM)_c$ related to the presence of a core hole on the emitting site, due to the intra-atomic character of the process, and an energy-dependent contribution ($FWHM_e$) accounting for the electron lifetime above E_F. The broadening values to be used are the following: $FWHM_g = 0.4$ eV (i.e., the experimental resolution); $FWHM_e = 0.1 \times |E - E_F|$ (eV) which has been previously found to nicely simulate BIS and XPS results;[7,18] and $FWHM_c = 0.4$ eV (see Ref. 13). The theoretical line shapes are displayed, after convolution with the mentioned broadening curves, in Fig. 1(b) together with the M_5-edge experimental results. The comparisons of Fig. 1(b) clearly put in evidence the good agreement of the experimental vs theoretical profiles. Due to the presence of the nearby M_4 edge ($\Delta_{s.o.} = 5.2$ eV for Pd, and 6 eV for Ag) and to the short range of the experimental calculation above E_F, the discrepancies visible for energies higher than about 4–5 eV are not really meaningful. Anyway, a detailed discussion of the line shapes is beyond the aim of this paper. Nevertheless, we would like to point out that the results of Fig. 1(b) enable us to interpret the $M_{4,5}$ near-edge XAS profiles of Pd and Ag mainly in terms of the p-related empty DOS within a single-particle framework, giving, moreover, the possibili-

ty of a precise and direct-hole-lifetime hole determination, due to the high resolution of the reported measurements. In fact, the contribution of the experimental resolution $FWHM_g$ to the total width, due to its Gaussian character, results in a negligible modification to the Lorentzian broadened ($FWHM_c + FWHM_e$) profile.

Similarly to the case of Pd and Ag for the Pd-Al alloys, a single-particle interpretation, in terms of *p*-related empty DOS, for the experimental line shapes related to the $M_{4,5}$ edges is appropriate. A joint XAS and BIS analysis reported on Pd-Al alloys[6] has shown very similar results for all the stoichiometries as far as the Pd empty *d*-projected DOS is concerned. This suggests that the effect of the 2*p* core hole, present in XAS but not in BIS, is vanishingly small. A similar situation has been theoretically explained to occur even in the case of Pd_2Si,[19] i.e., when Pd is coordinated with a semiconductor rather than a metallic partner. From this point of view, the case of a 3*d* core hole is even more favorable because of the much more pronounced localization of the 2*p* core hole.[20] Similarly, the experimental $M_{4,5}$ line shape of Pd_2Si (Ref. 10) has been recently interpreted within a one-particle scheme.
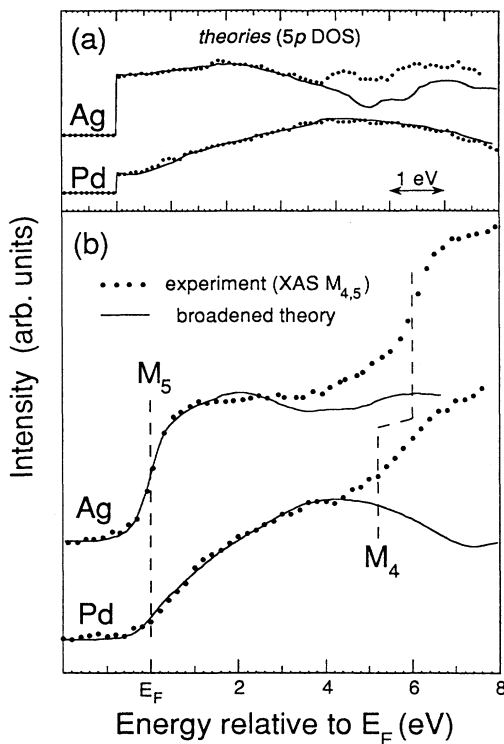

FIG. 1. (a) Theoretical 5*p* DOS's of Ag and Pd above the Fermi level. The dotted spectra are taken from Ref. 15. The solid-line spectra are taken from Refs. 17 and 16 for Ag and Pd, respectively. The Fermi level is represented by the edge. (b) Comparison between experimental XAS $M_{4,5}$ and calculated broadened spectra for Ag and Pd 5*p* DOS's above the Fermi level. The theoretical spectra are taken from Ref. 15 for both Ag and Pd. Both M_5 and M_4 edges are indicated in the experiment. For details about the broadening function, see text.

In Fig. 2, the $M_{4,5}$ edges for the three Pd-Al alloys are displayed together with the spectra of pure Pd and Ag used as a reference. All the spectra have been aligned, accounting for the different binding energies (BE's) of the pertinent $3d_{5/2}$ core level, as given in Ref. 3: 335.2 eV for Pd; 335.45 eV for $Pd_{0.85}Al_{0.15}$;[21] 337.05 eV for PdAl; 337.7 eV for $PdAl_3$; and 368.2 eV for Ag. From a careful analysis of the results shown in Fig. 2, the following observations can be drawn.

(i) On going from pure Pd to $Pd_{0.85}Al_{0.15}$, a dramatic change in the line shape occurs. In particular, the empty *p* DOS becomes higher close to E_F in the case of the alloy, as indicated by the much sharper behavior of the spectrum in the edge region. On the other hand, the evolution displayed by the 4*d* levels between Pd and $Pd_{1-x}Al_x$, as measured by XPS ($x = 10$), XAS ($x = 16$), and BIS ($x = 10$), i.e., with Al concentrations very similar to $Pd_{0.85}Al_{0.15}$, has a much smaller magnitude. In particular, these results mainly show a shift of about 0.2 eV away from the E_F of both occupied and the unoccupied *d*-derived states, representing a precursor state of the well-known hybridization gap. This gap becomes more evident at higher Al concentrations (e.g., for PdAl), as recently discussed in Ref. 8. Up to the 14% limit of solid solubility of Al in Pd, Pd-Al are substitutional alloys and therefore retain the Pd A_1 crystallographic structural type. In the case of $Pd_{0.85}Al_{0.15}$, the Pd-Pd coordination number goes from 12 in pure Pd to about 10. The different trend exhibited by the 5*p* vs 4*d* states can probably be attributed to the expected much higher delocalization of the *p* electrons, which allows a more efficient overlapping with the wave functions of the two nearest-neighbor Al atoms.
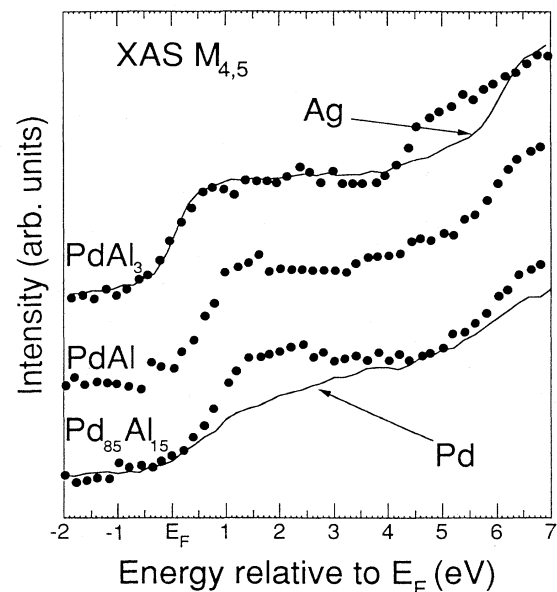
(ii) Further increasing of Pd-Al coordination from

FIG. 2. Experimental XAS $M_{4,5}$ spectra of Pd, $Pd_{0.85}Al_{0.15}$, PdAl, $PdAl_3$, and Ag.

$Pd_{0.85}Al_{0.15}$ for PdAl and PdAl$_3$ results in a more and more evident line-shape variation of the p-related DOS with respect to the pure Pd. In particular, a progressive filling of the region just above the edge is evidenced by the shift toward E_F of the centroids. The half maximum height moves from about 0.7 eV for $Pd_{0.85}Al_{0.15}$ to 0.5 eV for PdAl above E_F, whereas for PdAl$_3$ it is right at E_F.

(iii) When the highest Al concentration investigated is considered, a strong resemblance is found with Ag, as far as the empty p-projected DOS is concerned. In fact, the profiles of the Ag and the PdAl$_3$ spectra, depicted in Fig. 2 as overlapping, match very well apart from the different spin-orbit splitting of the involved core levels.

(iv) Despite the similar width of the M_5 edge for $Pd_{0.85}Al_{0.15}$, PdAl, and PdAl$_3$, only the last one can be interpreted as a real Fermi edge. Let us consider a step function and a smoother function with a straight-line transition of a given width (w). After applying to both of them the Lorentzian and the Gaussian broadenings, previously discussed for Pd and Ag, the two broadened line shapes are nearly indistinguishable up to w values of about 1 eV. This means that even if much sharper than the pure Pd profile, the near-edge profiles relative to both $Pd_{0.85}Al_{0.15}$ and PdAl can be related to smoother PDOS than the PdAl$_3$ Fermi-like edge.

(v) In the PdAl$_3$, profile the feature clearly seen at about 4.3 eV above E_F cannot be interpreted as the M_4 rise, considering that the spin-orbit splitting for PdAl$_3$ is 5.2 eV.[3] Actually, this behavior can be explained if one considers that the p band, for pure Pd and Ag, extends far above 10 eV relative to E_F.[15,16] We suggest that a structure in the PdAl$_3$ p-projected DOS is present, at about 4 eV, which obscures the M_4 edge at 5.2 eV.

In the following, we will discuss the progressive trend toward an Ag-like situation, shown by the Pd-Al alloys with increasing Al concentration, in connection with the behavior of the $4d$ levels. XPS results on Pd-Al alloys[2] show, even for the $4d$ states, an evolution of the total line-shape; its centroid, in fact, moves away from E_F, going from -2.3 eV for Pd and -4.1 eV for PdAl to -4.8 eV for PdAl$_3$, with a progressive depletion of the total DOS at E_F.[22] The PdAl$_3$ line shape is again very similar to that of a noble metal (i.e., with the d states well below E_F), apart from the nonvanishing d DOS above E_F as detected by BIS and XAS,[6] due to hybridization effects. This band filling is not attributed to a strong charge transfer but is mainly a hybridization effect, in agreement with the small variation of the d count and the small s-p overcompensation.[23] From this point of view, it seems reasonable to interpret the modification of the p states mainly in terms of an electronic redistribution rather than a charge-transfer effect. The parallel trend, at high Al concentrations, of Pd $4d$ and $5p$ states has to be taken into account. According to the general interpretation scheme, the d band of the alloy can be divided into three regions: a bonding and an antibonding region, interacting with the partner orbitals, which lie in an energy range below and above E_F, respectively; a region centered on the d-band peak, which is not hybridized with the partner orbitals and is considered not to be involved in the chemical bonding, called, therefore, "nonbonding." Quite recently,[7,8] the nonbonding behavior of these latter states has been questioned and their hole in the general distribution of electronic states outlined. In this framework, our results suggest a strong coupling between Pd p and d states that has never been considered up to now and shows the important role of p states in alloying formation. In particular, the nonbonding portion of the d states, which shows, as previously discussed, a noble-metal-like behavior, could be responsible of the strong redistribution of the p states. Another possible effect contributing to the evolution of the Pd $5p$ empty states can be related to hybridization with the nearby Al orbitals, in particular, those having p character. The $M_{4,5}$ profiles can *feel* some excitations to antibonding orbitals centered on the neighboring Al atoms, which exhibit some p character at the x-ray excited atoms, similarly to the case of $L_{2,3}$ XAS and energy-loss spectroscopy of the $3d$ transition metals.[24] It is interesting to note that in Pd$_2$Si, i.e., a compound whose electronic structure shows some similarity with the Pd-Al system, the presence of a Pd p-Si p coupling, which is not described by the bonding-antibonding picture, in the region of the Fermi level, has been theoretically[19] and experimentally[10] suggested.

In conclusion, we have reported a near-edge XAS investigation of the $M_{4,5}$ edges of Pd, $Pd_{0.85}Al_{0.15}$, PdAl, PdAl$_3$, and Ag. In the case of pure elements, the comparison with theoretical calculation shows how these spectra can be interpreted in terms of a single-particle p empty DOS via the $3d \rightarrow 5p$ absorption process. A precise measurement of the hole lifetime can therefore be performed, which gives a width of 0.5 ± 0.05 eV for the Ag $M_{4,5}$ level. The alloys show a strong progressive trend from the Pd to the Ag line shape with increasing Al concentration in the Pd matrix, which is already apparent at the lowest Al concentration investigated. The similarity of this evolution with that shown by the $4d$ levels, especially for high Al concentrations, indicates a strong correlation between Pd p and Pd d states. In particular, the involvement of electronic states having nonbonding d character is tentatively suggested. Also, the possibility of contributions due to Pd $5p$–Al $3p$ coupling is discussed. The evolution and the participation of the p states to the bonding formation is, therefore, stressed. Further theoretical efforts are needed to give a more complete description of the p contribution to the chemical bonding and to solve the d nonbonding dilemma, which we hope to stimulate with this work.

ACKNOWLEDGMENTS

[1]For extensive reviews, see, e.g., *Band Structure Spectroscopy of Metals and Alloys*, edited by D. J. Fabian and L. M. Watson (Academic, London, 1973); J. A. Alonso and N. H. March, in *Electrons in Metals and Alloys* (Academic, London, 1989).

[2]J. C. Fuggle, F. U. Hillebrecht, R. Zeller, Z. Zolnierek, P. A. Bennet, and C. Freiburg, Phys. Rev. B **27**, 2145 (1983).

[3]F. U. Hillebrecht, J. C. Fuggle, P. A. Bennet, Z. Zolnierek, and C. Freiburg, Phys. Rev. B **27**, 2179 (1983).

[4]P. A. Bennet, J. C. Fuggle, F. U. Hillebrecht, A. Lenselink, and G. A. Sawatzky, Phys. Rev. B **27**, 2194 (1983). XPS and Auger studies on $PdAl_3$ have also been reported by P. Weightman, and P. T. Andrews, J. Phys. C **13**, L815 (1980).

[5]S. C. Liu, J. W. Davenport, E. W. Plummer, D. M. Zehner, and G. W. Fernando, Phys. Rev. B **42**, 1582 (1990).

[6]D. D. Sarma, F. U. Hillebrecht, M. Campagna, C. Carbone, J. Nogami, I. Lindau, T. W. Barbee, L. Braicovich, I. Abbati, and B. De Michelis, Z. Phys. B **59**, 159 (1985).

[7]D. D. Sarma, W. Speier, R. Zeller, E. van Leuken, R. A. de Groot, and J. C. Fuggle, J. Phys. Condens. Matter **1**, 9131 (1989); S. W. Kortboyer, M. Grioni, W. Speier, R. Zeller, L. M. Watson, M. T. Gibson, F. Schäfers, and J. C. Fuggle, *ibid.* **1**, 5981 (1989).

[8]J. F. van Acker, E. W. Lindeyer, and J. C. Fuggle, J. Phys. Condens. Matter **3**, 9579 (1991).

[9]A. Bianconi, in *X-Ray Absorption: Principles, Applications, Techniques of Exafs, Sexafs and Xanes*, edited by D. C. Koningsberger and R. Prins (Wiley, New York, 1988), p. 573.

[10]G. Paolucci, K. C. Prince, G. Comelli, A. Santoni, and O. Bisi, Phys. Rev. B **41**, 3862 (1990).

[11]J. E. Müller, O. Jepsen, and J. W. Wilkins, Solid State Commun. **42**, 365 (1982).

[12]The semiempirical values, given as full width at half maximum, are FWHM $[K]$=6.24±0.13 eV, FWHM$[L_1]$ =4.93±0.6 eV, and FWHM$[K]$=6.75±0.14 eV, FWHM$[L_1]$=4.88±0.6 eV for Pd and Ag, respectively [see M. O. Krause, and J. H. Oliver, J. Phys. Chem. Ref. Data **8**, 329 (1979)].

[13]These values (FWHM's) are estimated from K. D. Sevier, in *Low Energy Electron Spectrometry* (Wiley-Interscience, New York, 1972), Chap. 6, p. 220. In particular, for the Ag M_5 edge, the broadening value of 0.34 eV has been indirectly found by subtracting the estimated L_3 width from the experimental $L\alpha_1$ (i.e., $L_3 \rightarrow M_5$ transition) emission line width [see L. G. Paratt, Phys. Rev. **54**, 99 (1938)].

[14]M. Surman, I. Cragg-Hine, J. Singh, B. J. Bowler, H. A. Padmore, D. Norman, A. L. Johnson, A. Atrei, W. K. Walter, D. A. King, R. Davis, K. G. Purcell, and G. Thornton, Rev. Sci. Instrum. **63**, 1341 (1992).

[15]Ag and Pd: D. A. Papaconstantopoulos, in *Handbook of the Band Structure of Elemental Solids* (Plenum, New York, 1986).

[16]Pd: O. Bisi (private communication); J. E. Muller, O. Jepsen, O. K. Andersen, and J. W. Wilkins, Phys. Rev. Lett. **40**, 720 (1978).

[17]Ag: T. K. Sham, Phys. Rev. B **31**, 1888 (1985).

[18]W. Speier, E. van Leuken, J. C. Fuggle, D. D. Sarma, L. Kumar, B. Dauth, and K. H. J. Buschow, Phys. Rev. B **39**, 6008 (1989).

[19]O. Bisi, O. Jepsen, and O. K. Andersen, Europhys. Lett. **1**, 149 (1986); Phys. Rev. B **36**, 9439 (1987).

[20]In the atomic approximation, the Pd $2p$ wave-function radial width [FWHM(Ψ_{2p})=0.06 Å] is four times smaller than the Pd $3d$ wave-function radial width [FWHM(Ψ_{3d})=0.24 Å]. See F. Herman and S. Skillman, in *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, NJ, 1963).

[21]Since in the case of $Pd_{0.85}Al_{0.15}$ the $3d_{5/2}$ BE is not reported in literature, we have used that of $Pd_{0.90}Al_{0.10}$. Small changes of this value are not relevant to the following discussion.

[22]In Ref. 8 the experimentally found total DOS at E_F given as total-states eV^{-1} atom^{-1} is 2.28 for Pd and 0.22 for PdAl.

[23]In Ref. 8 d counts of 8.74 and 8.86 are given for Pd and PdAl, respectively. In an alloy similar to PdAl [i.e., NiAl (Ref. 5)] an overcompensating s-p charge transfer is found: the Ni atoms gain some d character and lose more s and p electrons with a total transfer of about 0.1e^-. This picture agrees with the core-level shift analysis, which is interpreted as the result of a total charge transfer from Ni to Al atoms. On the other hand, the calculated electronic configuration, as given in Ref. 15, for elemental Ag and Pd, is $5p^{0.35}$ and $5p^{0.45}$, respectively with a difference of 0.1e^-.

[24]R. D. Leapman, L. A. Grunes, and P. L. Fejes, Phys. Rev. B **26**, 614 (1982).