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From x-ray-absorption near-edge structures to the *d*-hole population in Pd-Ag alloys

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The charge transfer upon alloying and the screening of the core hole in the x-ray absorption process in Pd-Ag alloys are discussed according to different models and with respect to different quantities. The charge transfers are analyzed using the first-principles electronic structure and spectrum calculations based on the linear muffin-tin orbitals method. Experimentally, both Pd and Ag gain *d* charge and lose non-*d* charge in Pd-Ag compared to pure Pd and Ag. The theoretical result agrees with the experimental one for Pd whereas the calculated charge transfer for Ag is in contradiction with the experimental result. This discrepancy is attributed to the differences in the electronic structure of Pd and Ag requiring new interpretation of the Ag x-ray-absorption near-edge structures of Pd-Ag alloys. [S0163-1829(99)02831-3]

I. INTRODUCTION

Bulk and surface properties of Pd-Ag alloys have recently attracted experimental interest.[1–3] The Pd-Ag alloy system has a complete miscibility and therefore acts as a prototype of a system whose electronic properties can be controllably altered. This is useful, e.g., in the understanding of the electronic properties of surfaces. Despite the fact that Pd-Ag is a relatively well-known system, the interpretation of its properties using spectroscopic data still calls for some attention.

Recently Coulthard and Sham[1] made a detailed experimental survey of the character and direction of charge transfer in Pd-Ag alloys in connection with the behavior of the alloy *d* band from a local perspective. They used Pd and Ag $L_{3,2}$- and L_1-edge x-ray-absorption near-edge structures (XANES) and x-ray photoemission spectra to analyze the charge transfer. $L_{3,2}$ XANES provides information on the unoccupied part of the *s* and *d* band (L_1 XANES is related with the *p* band) while photoemission provides information on the occupied part of the bands. According to their experiments, Coulthard and Sham concluded that in Pd-Ag both Pd and Ag gain *d* charge and lose non-*d* charge compared with pure Pd and Ag metals and the net charge transfer was argued to be from Ag to Pd in agreement with electronegativity arguments. The finding that the Pd sites in Pd-Ag alloys get more *d*-type charge with increasing Ag content is also supported by the Auger electron spectroscopic measurements.[2]

However, in order to make more definite conclusions about the charge transfer in alloys on the basis of spectroscopic data one should consider the following items in more detail. (i) The intensity of the considered $L_{3,2}$ XANES spectra is proportional to the square of the matrix element between the $2p$ and conduction states which means that the obtained spectra can probe only such a $4d$ charge transfer that occurs or at least produces a disturbance within those regions of the atom where the $2p$ state has significant intensity. A possible $4d$ charge transfer occuring in the other regions of an atom can be detected only indirectly or it cannot be detected at all. (ii) Changes in the localization of the $4d$ wave functions may lead to charge redistribution without any net charge transfer. However, these localization effects could also change the overlap of the $2p$ and $4d$ states in a similar way as the charge transfers do. Therefore, it is not straightforward to draw conclusions about possible charge transfers in alloys on the basis of experimental spectra alone.

II. METHOD

To shed more light on the interpretation problems above we perform first-principles electronic structure and x-ray spectrum calculations for Pd-Ag alloys. The electronic energy bands and wave functions needed in the charge transfer and spectrum calculations are obtained by using the scalar-relativistic linear muffin-tin orbitals (LMTO) method including the combined correction terms and the atomic sphere approximation.[4] For the details of the calculational procedure we refer to our earlier studies.[5] The absorption spectrum in the dipole approximation is given by

$$I_D(E) \propto \sum_{\mathbf{k}b(E_{\mathbf{k}b}>E_\mathrm{F})} |\langle \Phi | \hat{\boldsymbol{\epsilon}} \cdot \mathbf{r} | \Psi_{\mathbf{k}b} \rangle|^2 \delta(E_c - E_{\mathbf{k}b} + E), \quad (1)$$

where $E_{\mathbf{k}b}$, E_F, and E_c are, respectively, the energy of the one electron state with the wave vector **k** and band index *b*, the Fermi energy, and the energy of the core state, Φ and $\Psi_{\mathbf{k}b}$ are, respectively, the core state and the conduction-band state of an electron, $\hat{\boldsymbol{\epsilon}}$ is the polarization vector of the x-ray photon, and **r** is the position coordinate of the electron. The basis functions in the calculations consist of *s*, *p*, and *d* functions. The inclusion of the *f* states only leads to negligible effects to the considered quantities. The core-hole calculations are performed using a four atom unit cell. Increasing the number of atoms in the unit cell to 32 does not appreciably change the results at the Fermi level. In reality, the considered Pd-Ag alloys are substitutionally disordered intermetallic alloys. In the calculations, however, the crystal structure of these alloys is simulated by the conventional repeated supercell technique.

III. RESULTS AND DISCUSSION

A. Screening of the core hole

At first, it is useful to consider problems related with the interpretation of x-ray absorption spectra in a general level. Good presentation of the various phenomena involved in the core level spectroscopies is given, e.g., by Fuggle.[6] In addition to the usual problems related with the exchange-correlation potential of the electron gas there is an additional problem in the absorption process due to the existence of the core hole. When an x-ray photon is absorbed by an electron in a core level the electron makes a transition to a higher unoccupied level leaving the core hole behind. This core hole has an effective charge $+1$ screened by the valence electrons. During the screening the valence and conduction bands are deformed and the amount and character of the deformation depends on the system considered. To calculate the electronic structure of the screened system various models have been used. In the $Z+1$ approximation the perturbation of the core hole is approximated by replacing the absorbing atom by an atom whose atomic number is one unit greater than that of the original atom. In the core-hole approximation the band-structure calculation is performed for a system in which an electron of an absorbing atom has been transferred from the core level to the Fermi level.[7]

For simple metals the experimental spectra related with a core hole (absorption and Auger spectra) are usually accounted for better by calculations using the $Z+1$ or core-hole approximation than by ground-state calculations.[8] For transition metals the situation is not so straightforward. Our core-hole calculation for Pd and PdAg leads to the complete filling of the 4*d* band and consequently the disappearing of the peak of the empty *d* states just above the Fermi level, which is in distinct contrast with the measurements of Coulthard and Sham.[1] For Ni, which belongs to the same column in the Periodic Table as Pd, both the electron-energy-loss spectra (EELS) and bremsstrahlung isochromatic spectra (BIS) show a similar significant peak near the edge.[9] The BIS is related with a neutral atom and the EELS corresponds to an atom with a core hole. Thus, theoretical and experimental results suggest that at the end of the transition metal series the effect of the core hole on the *d* density of states (DOS) around the Fermi level is less pronounced than at the beginning of the transition-metal series. Since we are interested in the *d* states of Pd-Ag alloys near the Fermi level we can justifiably use the ground-state calculations to interpret the experimental data.

B. Charge transfer

In the following, we will focus on the basic assumption made in analyzing the XANES data of Pd-Ag alloys namely that a change in the white-line intensity at the $L_{3,2}$ edge allows us to probe directly the effect of alloying on the *d*-hole population of Pd-Ag alloys. Because the physical properties of the pure constituents of an alloy form the basis of understanding of the properties of alloys, we begin our discussion by summarizing the basic electronic properties of pure Pd and Ag (see, e.g., Refs. 10–12). The number of valence electrons in Pd and Ag is 10 and 11, respectively. Resolving the electronic states of the valence electrons into *s*, *p*, and *d* components shows that both metals have approximately the same amount of non-*d*-type electrons (1.05 in Pd and 1.00 in Ag) indicating that Ag has approximately one *d* electron more than Pd. In Pd, part of the antibonding states of the *d* band are unoccupied leading to the slightly smaller atomic volume of Pd compared to that of Ag. The experimental lattice parameter (both metals have fcc structure) is 7.3524 and 7.7205 a.u. for Pd and Ag, respectively.[13] Due to the above difference in the atomic volumes the average valence electron density in Pd is higher than that in Ag despite the larger valence electron number in Ag. The average density of valence electrons is $0.101/\mathrm{a.u.}^3$ and $0.096/\mathrm{a.u.}^3$ for Pd and Ag, respectively. Due to the larger nuclear charge and the larger number of antibonding *d* states of Ag the *d*-type valence charge is more localized in Ag than in Pd.[12]

Conventionally the charge transfer between the atomic sites in alloys is defined with respect to certain volumes associated with the considered atomic sites. In our study we choose these volumes to be the Wigner-Seitz (WS) spheres of the constituents of the alloy. At first, we discuss the net charge transfer in Pd-Ag alloys using a simple model based on the pure metal data. In this model, which we call a rigid charge-density model (RCDM), we assume that the effective valence charge density of pure metals can be represented by the superposition of uniform charge densities located in the corresponding WS spheres. The charge density of an alloy is then formed by attaching the charged WS spheres of the pure metals to the exact atomic positions of the alloy. The obtained charge transfer in the alloy, compared to the pure metal case, is then produced by the change of the overlapping of the rigid atomic charge densities, which is due to the possible change in the lattice parameter upon alloying. In our case, when Pd is diluted with Ag the lattice parameter (or

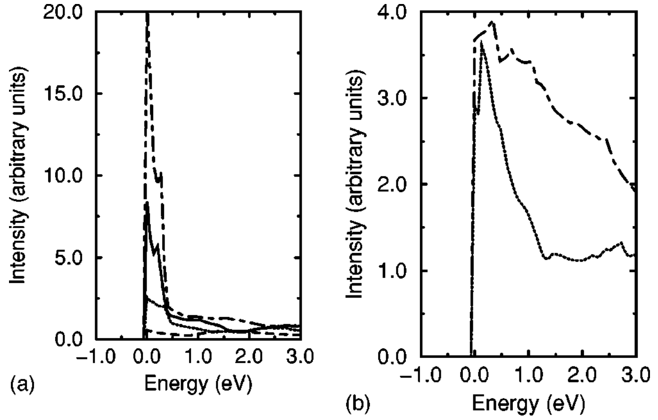

FIG. 1. Calculated x-ray absorption L_3 edges of Pd (a) and Ag (b) in Pd-Ag alloys. Curves from top to bottom: (a) Pd, Pd_3Ag, PdAg and $PdAg_3$, (b) Ag and PdAg.

WS radius) of the alloy increases almost linearly from the pure Pd value to the pure Ag value as a function of Ag content.[13] Before using the RCDM, one has to decide what is the proper effective charge density to be attached to the pure metals. For instance, in the case of Pd and Ag one could think that the total effective charge within the WS spheres could be the amount of itinerant $5s$ and $5p$ valence electrons or the amount of $5s$, $5p$, and $4d$ valence electrons or something in between. The best agreement with the LMTO results is obtained if the itinerant non-*d* valence electrons are used to produce the charge density in RCDM (Table I).

Unfortunately, the simple model used above does not tell us anything about the possible complex interplay between the different symmetries of the charge density upon alloying. However, this information is essential in interpreting the spectral data of alloys because due to the selection rules the experimental spectra are related with the different angular momentum components of the electronic states. In order to understand the charge transfer in Pd-Ag in more detail we have to use more sophisticated methods. In the following, the first-principles LMTO calculations are used to analyze the charge transfer in Pd-Ag alloys further. According to our calculations Pd gains *d* charge and loses non-*d* charge upon dilution with Ag. Ag loses *d* charge and its non-*d* charge behaves nonmonotonically in such a way that the total charge transfer in Ag is practically constant upon dilution with Pd. While our results for Pd are consistent with the conclusions made by Coulthard and Sham (see Table I), our results for Ag differ significantly from the conclusions derived from the experiments. According to Coulthard and Sham the partial charge in Ag behaves in a way similar to that in Pd. Whether this disagreement is real or it is only due

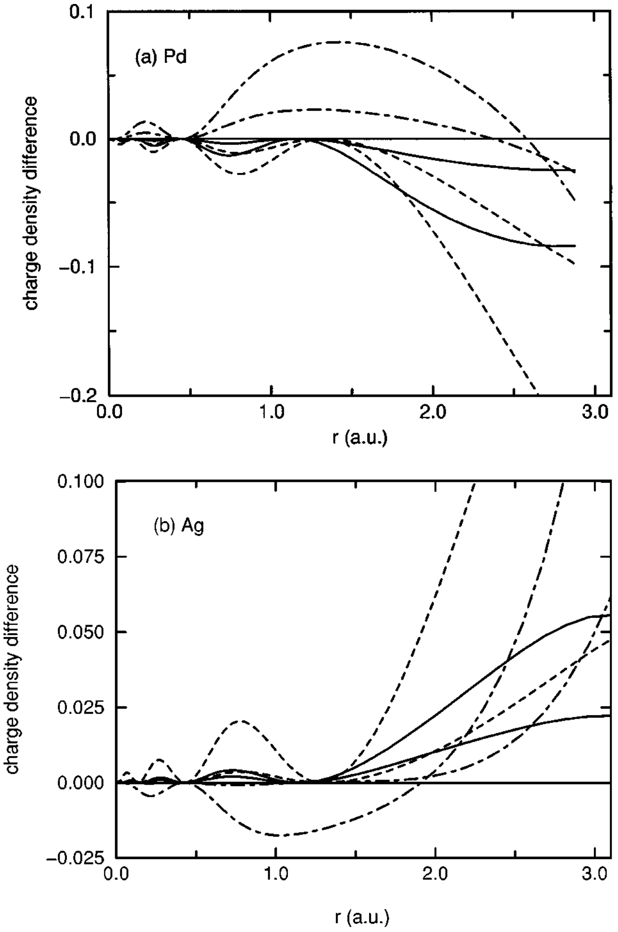

FIG. 2. The charge-density differences (alloy minus pure element) for Pd (a) and Ag (b). Solid line *s*-, dashed line *p*-, and chain-dotted line *d*-type charge. The alloys considered are Pd_3Ag and $PdAg_3$. The curves correspond to the alloys in the following way: for Pd the *s* and *p* charge decrease and the *d* charge increases with increasing Ag content, for Ag the *s* and *p* charge decrease with decreasing Pd content whereas the *d* charge increases in the inner part of the WS sphere and decreases in the outer part of the WS sphere.

TABLE I. Charge transfer in Pd-Ag alloys. ΔQ_{Pd}: the change of the total charge within the Pd WS sphere (S) (Ref. 13) compared with the pure Pd case. $\Delta Q_{\mathrm{X}}^{y}$: the change of the y charge within the X WS sphere compared to pure X case ($X=$Pd or Ag). Results are given in numbers of electrons. In RCDM the charge density consists of $5s$ and $5p$ electrons. Experimental results are taken from Ref. 1.

		ΔQ_{Pd}		$\Delta Q_{\mathrm{Pd}}^{d}$		$\Delta Q_{\mathrm{Pd}}^{\text{non-}d}$	$\Delta Q_{\mathrm{Ag}}^{d}$	$\Delta Q_{\mathrm{Ag}}^{\text{non-}d}$
At.% Ag	S (a.u.)	RCDM	LMTO	Exp.	LMTO	LMTO	LMTO	LMTO
0	2.8733	0.00	0.00	0.00	0.00	0.00		
25	2.9044	0.05	0.02	0.12	0.07	−0.06	−0.09	0.04
50	2.9374	0.11	0.07	0.22	0.20	−0.13	−0.06	−0.00
75	2.9745	0.18	0.11	0.24	0.26	−0.14	−0.03	−0.01
100	3.0171						0.00	0.00

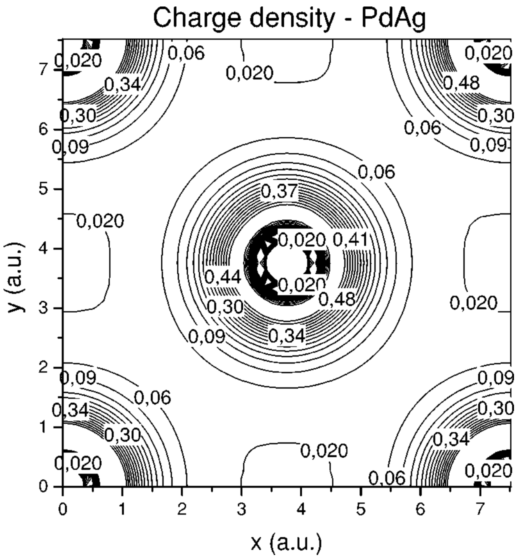

FIG. 3. The valence charge density of PdAg alloy in the (100) plane (Pd in the middle and Ag in the corner).

to different definitions for charge transfer used in the calculations and in the analysis of the spectral properties is to be solved.

In our calculations, we define the charge transfer to be the change in the number of certain type electrons within the WS sphere. Coulthard and Sham relate the charge transfer to the change in the intensity of the white line of the absorption spectra. This intensity depends on the number of unoccupied electronic states and the transition probability for an electron to transfer from a core state to an unoccupied state. The calculated L_3 absorption edges of Pd and Ag (Fig. 1) agree quite well with the experimental spectra[1] suggesting that the disagreement between the theoretical and experimental results for the charge transfer in Ag sites in Pd-Ag alloys is due to different interpretations of the spectra. The DOS data extracted from the spectrum measurements can be related to the number of electronic states through Eq. (1), but the problem is to relate the obtained number to a specific region in space. Of course, the induced charge transfer crucially depends on the spatial region used in the consideration. This mapping from the number of electrons to the corresponding spatial regions in an alloy is determined by the matrix element between the core state and the conduction state involved in the particular absorption process [see Eq. (1)]. Thus, the charge-transfer data obtained from the measurements of absorption spectra cannot be compared directly with the calculated net charge transfers within WS spheres. Instead, one needs to consider the charge-transfer distribution within the WS sphere.

C. Charge distributions and electron localization function

A more informative picture of the charge transfer in Pd-Ag alloys can be obtained if one considers the charge density of the alloy as a function of position coordinate instead of a single number specifying the excess or deficiency of the electronic charge within the WS spheres. The effect of alloying on the charge distribution can be illustrated by subtracting from the charge density of the alloy the corresponding charge density of the pure metal. As Fig. 2(a) shows, the result for Pd is quite clear and it is in agreement with the results of Coulthard and Sham.[1] Pd gains *d* charge upon alloying except at the outer regions of the WS sphere where the *d* charge density decreases. The non-*d* charge density of Pd decreases upon alloying within the whole WS sphere. Pd in Pd-Ag is an example of a case with a straightforward

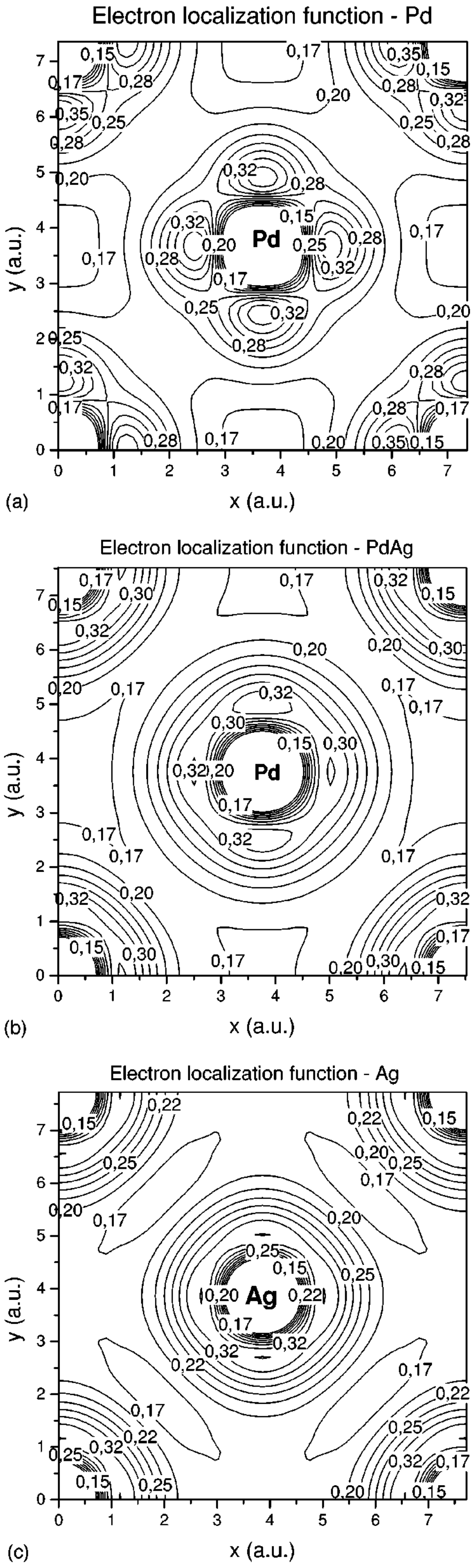

FIG. 4. The valence ELF of (a) pure Pd, (b) PdAg alloy, and (c) pure Ag in the (100) plane.

interpretation of the charge transfer: the spectral data, net charge within the WS sphere, and the charge distribution, they all lead to the same conclusion, Pd gains *d* and loses non-*d* charge upon alloying with Ag.

The situation with Ag, however, is more complicated. The *d* charge density decreases in the inner part of the WS sphere, but increases in the outer part. In this case, the spectral data, net charge within the WS sphere, and the charge distribution lead to the contradictory interpretation of the charge transfer at Ag site. When considering the non-*d* charge at Ag site the situation is not any simpler. Figure 2(b) shows that the non-*d* charge increases upon alloying, which is in contradiction with the conclusion made according to the spectral data that predicts decreasing non-*d* charge upon alloying. The calculated net non-*d* charge within the WS sphere is practically constant. This can be explained by the decreasing of the volume of the Ag WS sphere upon alloying compensating the effect of the increase in the non-*d* charge density in Ag. Summarizing from Fig. 2, the general trend of the electronic density in Pd-Ag alloys with increasing Ag content is that the density of the non-*d* charge decreases at both atomic sites. This can be related to the increasing of the volume of the alloy with increasing Ag content. At the same time the *d* charge gets more localized, i.e., the *d* charge density increases in the inner part of the WS spheres and decreases in the outer parts of the WS spheres.

To analyze the charge distribution and bonding between the atoms of an alloy two-dimensional charge-density plots are usually considered. As Fig. 3 shows there are only minor differences between the valence charge densities of the Pd and Ag sites in the PdAg alloy. Moreover, there are only small differences between the charge densities of the same atomic type in the alloy and in the pure elemental metal. To see more clearly the effects of alloying on the charge density one has to consider, instead of the charge density, a quantity that is related more directly to the variations of the charge density. One such possible quantity is the electron localization function[14] (ELF) which depends on the gradients of the charge density and wave functions

$$\mathrm{ELF}=\left\{1+\left[0.3483\rho^{-5/3}\left(\sum_{\mathbf{k}b}|\nabla\Psi_{\mathbf{k}b}|^2-\frac{1}{8}|\nabla\rho|^2/\rho\right)\right]^2\right\}^{-1}, \tag{2}$$

where ρ is the electron density. In Fig. 4, the valence ELF of pure Pd, the PdAg alloy, and pure Ag is shown. The ELF of pure Pd is more anisotropic than that of pure Ag. In the central part of the atoms the valence ELF has a minimum due to the small value of the valence charge density and due to the high value of the gradients of the valence wave functions in the core region. As the distance from the center of the atom increases the ELF reaches a spherical region, which in the case of Pd contains distinctly separated maxima pointing out to the hollow sites of the lattice. This region of the maxima in the ELF of Pd and Ag can be related to the maximum of the 4*d* radial wave function. In the region outside the atomic cores the ELF of Pd shows stronger bonding character between the nearest-neighbor atoms than the ELF of Ag. The anisotropic structure of the ELF in Pd can be related to the partly unfilled 4*d* band of Pd. Thus, the structures in the ELF can be related to the *d*-hole population and the nodal structure of the valence wave functions. In the ELF distinct effects of alloying can be seen. The filling of the 4*d* band of Pd in the PdAg alloy is manifested as the decreasing of the anisotropy of the ELF at Pd sites and the decreasing of the bonding character between the atoms in the Pd-Ag plane of PdAg compared to pure Pd. The corresponding alloying effects in the ELF at Ag sites are small.

IV. CONCLUSIONS

The electronic structure of Pd and Ag differs with respect to the position of the *d* band. Pd has partially filled *d* band whereas the *d* band of Ag is completely filled and has the binding energy of several electron volts. When alloying Pd with Ag the experiments show that the top of the 4*d* band of Pd in Pd-Ag alloys is shifted to lower energies with increasing Ag content. This is manifested as the increase of the occupation of the Pd 4*d* band. Our calculated result for the increase of the *d*-type charge in Pd with increasing Ag content agrees qualitatively with this result.

For Ag our results, however, are in contradiction with the conclusions drawn from the experiments. Our results show that the total *d*-type charge of Ag decreases somewhat upon alloying with Pd. Conclusions drawn from the charge transfers are not straightforward since both the expansion of the wave functions into the *s*, *p*, and *d* components related to the different atoms and the volume of an alloy change from the values for pure metals upon alloying. Furthermore, the charge transfer does not need to have the same sign through the whole WS sphere. Actually, in the outer part of the Ag WS sphere the alloying increases the *d*-charge density while the total *d* charge of Ag decreases. In the case of Pd-Ag alloys, the experimental result of the decreasing of the white line in Ag should be related to the charge transfer from Ag to Pd due to the alloying and change of the volume of the crystal rather than the charge redistribution in the Ag site. Thus, the interpretation of the absorption spectra of alloys with regard to the charge transfer requires a detailed spectrum calculation combined with the charge-density considerations.

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