Charge Redistribution in Pd-Ag Alloys from a Local Perspective

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Using Pd and Ag $L_{3,2}$-edge x-ray-absorption near edge structures (XANES) and x-ray photoemission spectroscopy, we have investigated the charge distribution in a series of Pd-Ag alloys (Pd_3Ag, PdAg, and $PdAg_3$) from a local perspective. It is found that, relative to the pure element, both Pd and Ag gain *d* and lose non-*d* (*s* and *p*) charge upon alloying. The results are discussed in terms of band filling, rehybridization, electronegativity, and electroneutrality considerations. The possibility of using the $L_{3,2}$-edge XANES white line to circumvent the need of an appropriate volume for charge transfer discussions and for other applications are noted. [S0031-9007(96)01801-7]

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The electronic properties of 4*d* noble metals, Pd and Ag, are determined largely by their band structure, particularly the energy distribution of the *d* electrons and the interplay between the *d* and the non-*d* (*s* and *p*) conduction electrons [1]. Thus *d*-charge redistribution upon alloy formation has a profound effect on the electronic behavior of the alloy. It is generally recognized that the Pd *d* band extends above the Fermi level, ϵ_F, and exhibits high unoccupied densities of *d* states at the Fermi level while the Ag *d* band is entirely below ϵ_F [2]. Experimentally, the occupied portion of the *d* band can be studied with photoemission, and, to a lesser extent, x-ray emission techniques, while the unoccupied densities of states of *d* character can be investigated with the $L_{3,2}$-edge x-ray-absorption near edge structure (XANES). This is because $L_{3,2}$ XANES probes the *d* holes via dipole transitions. It has been shown that, owing to the presence of localized densities of states (DOS) of the unoccupied *d* band at the Fermi level, the Pd $L_{3,2}$-edge XANES exhibits an intense spike (commonly known as a white line) at the onset of the $L_{3,2}$-edge XANES, while the XANES of Ag, of which the *d* band is nominally full, does not [3]. In the latter, however, close examination reveals that there exist some unoccupied states of 5*d* character above the Fermi level in Ag as the result of *s*-*p*-*d* rehybridization [4].

The Pd-Ag alloy system, which has complete miscibility, fcc structure, and negligible volume effects, is of particular interest in that the center of gravity of the *d* band of the pure elements, which can be determined by an atomiclike one-electron energy (ϵ_d), is well separated and that Pd-Ag alloy is known to have two separate *d*-band components which closely correspond to that of the pure constituents [5,6]. The energy position of ϵ_d changes only slightly in the alloys, although the individual *d* component narrows as the constituent becomes more dilute. In this paper, we examine *the nature and the direction of charge transfer in Pd-Ag alloys in connection with the behavior of the alloy d band from a local perspective.* Pd and Ag $L_{3,2}$-edge XANES [3,7], which is ideally suited as a local probe for the study of unoccupied *d* states above the Fermi level in Pd-Ag alloys, was used together with photoemission in this study. A change in the white-line intensity at the $L_{3,2}$ edge upon alloying provides information on the change of *d*-hole population (*p*-*d* is the dominant transition) at the site of interest while photoemission provides information for the occupied portion of the *d* band.

The most commonly used criterion in charge redistribution studies is the electronegativity difference between the constituents while the parameters relevant to the *d*-band behavior are the width, energy position and intensity of the overall and/or individual components of the alloy *d* band, as well as core level shifts, as observed in photoemission measurements. In addition, an appropriate volume must be chosen for the atomic site of the constituents of interest in a binary system for charge transfer discussion (muffin-tin or Wigner-Seitz spheres are commonly used as volumes assigned to the constituents).

Is it often argued that, in a binary system, the more electronegative constituent tends to gain charge, whereas the other loses charge. Thus charge flow is expected from Ag to Pd in Pd-Ag alloys since Pd is more electronegative than Ag. While this argument generally works well for compounds of nontransition elements, it has been shown that, more often than not, complications arise in metallic alloys of metals with full or nearly full *d* bands [1,3,4]. When electroneutrality is taken into account, the overall charge transfer on and off the site must be small since each constituent tends to maintain charge neutrality locally. The problem with electronegativity is that it does not deal with the nature of the charge (s, p, d, etc.) explicitly. In the case of Au alloys, charge redistribution can only be explained with a charge compensation (rehybridization) mechanism in which the transfer of the more localized *d* (off the Au site) and the itinerant *s* and *p* conduction electrons (onto the Au site) is in opposite directions. A Pd and Ag $L_{3,2}$-edge XANES study will allow us to probe directly the effect of alloying on the *d*-hole population at both the Pd and Ag sites in the alloy.

High purity Pd and Ag metals used in this study were obtained commercially, and Pd-Ag alloys, $Pd_{0.25}Ag_{0.75}$, $Pd_{0.5}Ag_{0.5}$, and $Pd_{0.25}Ag_{0.75}$ (henceforth denoted Pd_3Ag, PdAg, and $PdAg_3$, respectively), were prepared by the Materials Preparation Group at McMaster University using standard procedures. $L_{3,2}$-edge XANES measurements were carried out in a vacuum chamber in a total electron yield mode at the double crystal monochromator beam line of the Canadian Synchrotron Radiation Facility located at the Synchrotron Radiation Center (SRC), University of Wisconsin-Madison. InSb(111) was used as monochromator crystals. SRC operated at 800 MeV with 200 mA at injection. We have also carried out photoemission measurements of the core levels and valence bands on the very samples using a monochromatized Al $K\alpha$ source.

Figure 1 shows a set of XANES spectra covering the Pd $L_{3,2}$- and Ag $L_{3,2}$-edge region of PdAg and the individual elements. Figure 2 shows the Pd L_3-edge XANES for Pd, Pd_3Ag, PdAg, and $PdAg_3$ as well as the Ag L_3-edge XANES for PdAg and Ag metal. We have removed the Pd L_2 contribution to the Ag L_3 edge by subtracting from it the Pd L_3 x-ray-absorption fine structure (XAFS) properly aligned and scaled to represent the Pd L_2 edge (right panel). From Fig. 2, two interesting features are noted. First, the white-line intensity at the Pd L_3 edge decreases significantly as Pd becomes more dilute. Second, close examination of the Ag L_3 edge for PdAg reveals a noticeable decrease in intensity just above the edge as the concentration of Ag decreases. Similar behavior was also observed for other alloys and at the Pd L_2 and Ag L_2 edge. Using the Ag L_3-edge XANES of Ag metal (aligned at $E_0 = 0$ eV) as a reference, we obtained the integrated area ($\sim$10 eV above the threshold) [4] under the difference curve between the alloy and pure Ag and estimates of d-hole counts at both the Pd and Ag sites for all samples [8]. This procedure assumes that the d-hole count for both Pd and Ag metal is known theoretically [9], that the dipole transition matrix element for Pd and Ag are the same [10], and that the final state effect is the same for all alloys [11].

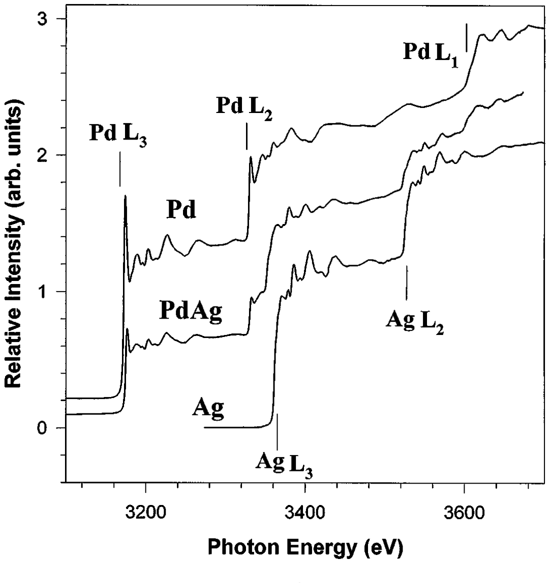

FIG. 1. L-edge XANES for Pd, PdAg, and Ag.

Figure 3 shows the corresponding valence band of the same samples, where the individual d bands of the constituents can be easily identified as reported previously [5,6]. These results are accompanied by a $3d$ core level shift (to lower binding) of -0.2 to -0.4 eV for the Pd and -0.2 to -0.8 eV for the Ag, suggesting that both sites gain charge. The individual d-band narrowing is the result of reduced coordination numbers of like atoms upon dilution. The trend for the width of the occupied d-band component is to be correlated with the change of d-charge counts. It turns out that the Pd/Ag d band gets filled and becomes more localized upon dilution.

The results shown in Figs. 2 and 3 strongly suggest that, in PdAg, both Pd and Ag gain d charge. This is evident from the decrease of white-line intensity at the $L_{3,2}$ edge (hence d-hole population) for both elements upon dilution [8]. It has been well established that within the one-electron approximation the white-line intensity is a function of the square of the dipole transition matrix element and the unoccupied DOS of d character (d holes) [12]. Assuming that the transition matrix element remains essentially constant between the pure metal and the alloys, the area under the white line at the $L_{3,2}$ edge is directly proportional to the $d_{5/2,3/2}$-hole count at the Pd/Ag atom in the alloys [12].

The white-line intensity difference and d-band width systematics for Pd and Ag are summarized in Fig. 4 as a function of composition. It is apparent from these correlations that the Pd d band gets filled and becomes more localized as Pd is diluted in Ag. Using the d-hole count of 1.784 and 0.856 for Pd and Ag metal,

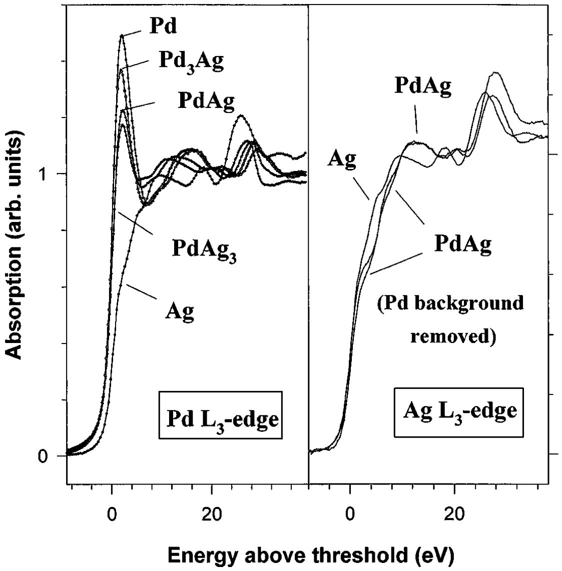

FIG. 2. Left panel: Pd L_3-edge XANES systematics for the alloys relative to the elements, spectra are normalized and calibrated relative to the threshold: Right panel: Ag L_3-edge XANES for Ag and PdAg before and after the removal of Pd contributions, other alloys XANES, which also exhibit reduced intensity just above the edge relative to Ag, are not shown for clarity.

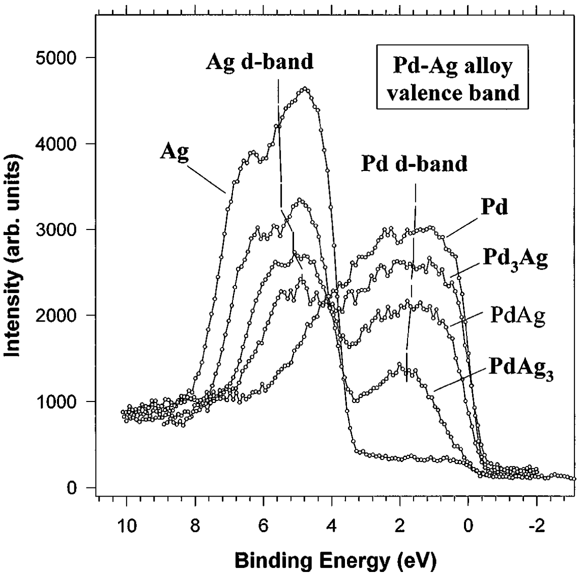

FIG. 3. X-ray photoemission spectroscopy valence band spectra for the alloys and elements at ~0.7 eV resolution. The bar marks the centroid (±0.2 eV) of the individual *d* bands. Bandwidths are defined with the rising edge of the *d* band whenever possible.

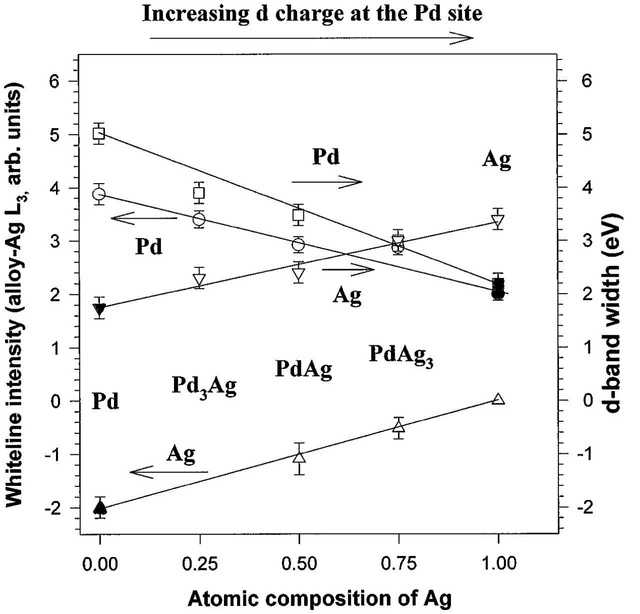

FIG. 4. Correlations of the white-line intensity difference between alloy and Ag L_3-edge XANES (Fig. 2) and the *d*-band width of individual components (Fig. 3) with composition. Solid symbols denote the extrapolated values for infinite dilution.

respectively, from a recent calculation of Lu, Wei, and Zunger [9], and assuming the statistical distribution of the $d_{5/2}$ and $d_{3/2}$ holes, we estimate the *d*-hole count at the Pd site to be 1.66, 1.56, and 1.54 (within 5%) for Pd$_3$Ag, PdAg, and PdAg$_3$, respectively [13]. The result of the white-line correlations indicates that, even at infinite dilution (Fig. 4, solid symbols), the Pd *d* orbitals would not be completely filled (*d*-hole count ~1.33). Incidentally, the *d*-band width would not vanish at infinite dilution as the result of *d* electron scattering, in agreement with previous findings [6].

It is also interesting to compare our finding with the calculation of Lu, Wei, and Zunger [9] on the electron distribution for AgPd alloy. They found that, within the muffin-tin sphere, Pd in PdAg gains a significant amount of *d* charge (0.086*e*) relative to the pure metal, in qualitative agreement with our observation (0.23*e*). The calculated *d*-charge transfer at the Ag site is very small ($-0.007e$) but in the opposite direction to our observation. We found that Ag gains *d* charge, although the *d*-hole count cannot be quantified with confidence since the Ag L_3-edge absorption is complicated by the Pd XAFS. The observation that both Pd and Ag in the alloys gain *d* charge indicates immediately that there must be a loss of non-*d* conduction electron counts at one or both sites to conserve charge. We argue that the more electropositive Ag would lose net charge, therefore, it must lose non-*d* charge which is partially compensated by the *d*-charge gain. In the case of Pd, although its significant change in white-line intensity clearly indicates a gain of *d* charge, the fact that its 3*d* core level shifts have a smaller range compared to that of Ag, and that its *d* band shifts little, suggests some non-*d* charge depletion at the Pd site. Thus the picture we have for the Pd-Ag alloy is one in which both Pd and Ag gain *d* and lose non-*d* charge; the charge loss in Ag is only partially compensated by the *d*-charge gain, and the overall charge redistribution is in accord with electronegativity arguments. This result is in qualitative agreement with the calculation [9] which predicts that both Pd and Ag would lose *s* and *p* charge in the PdAg alloy and that Ag loses net charge. The depletion of *p* charge in Pd is also evident from the increase in absorption intensity above the metal L_1 edge (*s* to *p* dipole transition) as shown in Fig. 5 for PdAg. The Ag L_1 edge changes little within the experimental uncertainty. This may suggest that the depleted charge at the Ag site is of primarily *s* character.

Finally, it would be interesting to compare the PdAg results with that of AuAg [4,9]. In the latter, it was found that Au loses *d* charge and Ag gains *d* charge. The behavior of Au is in contrast to that of Pd despite its larger electronegativity. We attribute this difference to the fact that Au nominally has a full *d* band and that spin-orbit interaction for the Au 5*d* is comparable to that of band effects and has a significant impact on the charge redistribution.

In summary, we have reported that both Pd and Ag gain *d* charge and lose non-*d* charge upon dilution in each other, and that the conclusion of *d*-charge gain can be arrived at solely from experimental observation. Thus the $L_{3,2}$-edge XANES white line may be used to study *d*-charge redistribution in 4*d* elements and their compounds directly, circumventing the need to define an appropriate volume for the discussion of charge transfer; this is plausible since the 4*d* radial wave function is well within the Wigner-Seitz radius [10]. The XANES and photoemission results

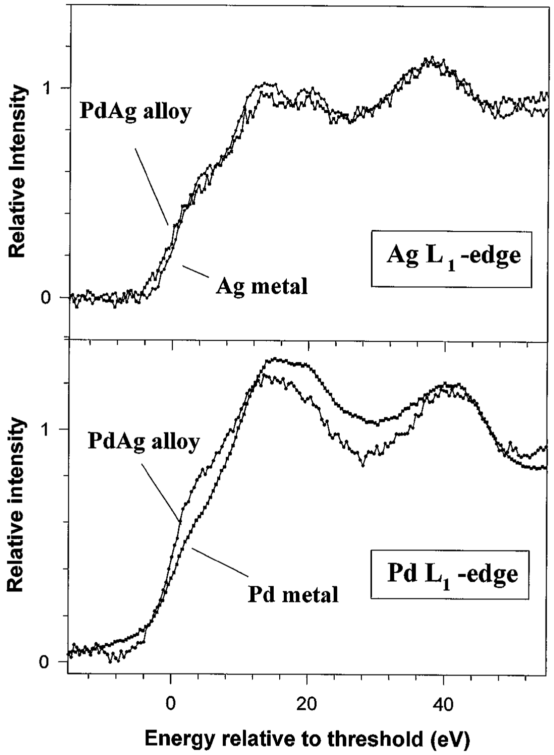

FIG. 5. Pd and Ag L_1-edge XANES for PdAg compared with the elements. The alloy exhibits a more intense jump just above the Pd edge ($\sim$10 eV) indicating an increase in p-hole count at the Pd site (p-charge depletion) while the Ag L_1 edge changes little.

reported here clearly indicate that a charge compensation mechanism operates in these alloys. It is interesting to note that these results can be used to correlate optical properties, Fermi surface behavior, Friedel charge screening, as well as mechanical and thermodynamic properties of these alloys. In addition, this system may be used to explore the validity of the high resolution, narrow-window Auger yield XANES (radiationless Raman x-ray scattering) [14] and x-ray magnetic circular dichroism of 4d noble metal alloys. Some of these issues will be dealt with elsewhere.

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