Catalysis Letters 30 (1995) 1–10

X-ray absorption studies of the electronic structures of Pd–Ag and Pd–Au alloys

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Received 8 July 1994; accepted 30 August 1994

Information on the number of unoccupied d-states in the valence band of a metal can be obtained from a study of the intensities of the X-ray absorption threshold resonances associated with L_{III} and L_{II} absorption edges. Such resonances, which are attributed to excitations of electrons from 2p core levels to the unoccupied d-states, have been investigated for both Pd–Ag and Pd–Au alloys over the same range of composition. The spectra were obtained from measurements of the intensity of emission of electrons (total electron yields) from powder samples. This method avoids experimental artifacts associated with sample thickness effects of the type encountered with X-ray transmission or fluorescence measurements. The attenuating effect of the Group IB metal on the resonances of palladium in the alloys was much smaller than the effect predicted by the "rigid-band" model of the electronic structure, but substantially greater than that previously observed for Ni–Cu alloys.

Keywords: Pd–Ag and Pd–Au alloys: (1) electronic structure of; (2) rigid band model of; (3) unfilled palladium d-states of; (4) X-ray absorption by; (5) absorption threshold resonances of; (6) L_{III} and L_{II} absorption edges of

1. Introduction

Metal alloys have long been of interest for studies of the "electronic factor" in catalysis by metals [1–3]. For alloys consisting of a Group VIII metal and a Group IB metal (e.g., Ni–Cu, Pd–Ag, or Pd–Au), it was proposed in an early model of the electronic structure that the two components share a common d-band which becomes increasingly filled with electrons as the amount of the IB metal increases [4,5]. Since pure Pd and Ni have approximately 0.6 unoccupied d-states per atom [6], the model predicts complete filling of the d-band when an alloy of either of these metals with a IB metal contains about 60 at% of the latter.

This model, known as the "rigid-band" model, was widely accepted for many years because of its success in accounting for magnetic properties of the alloys. Eventually, however, the results of a variety of types of investigations cast doubt on the validity of the model [7–14]. For example, photoemission studies of Ni–Cu alloys indicated that the two components of the alloys possessed separate d-bands instead of the common d-band envisioned in the model [9–11]. However, these investigations did not provide information on the degree of filling of the d-band of the Group VIII metal as a function of the amount of IB metal in the alloy.

Such information can be obtained from studies of L_{III} and L_{II} X-ray absorption edges [15–18]. The absorption threshold resonances at these edges, which are commonly called "white lines" [19], are due to excitation of electrons from 2p core levels to unoccupied d-states in the valence band [20]. Cordts et al. have made X-ray transmission measurements on several Ni–Cu [15] and Pd–Ag [16] foils, and concluded that the influence of the IB metal on the number of unoccupied d-states of the Group VIII metal was significantly different for the two alloy systems. In arriving at their conclusions, these investigators made appropriate corrections for the sample "thickness effect" [21–23]. While the correction procedure was clearly reasonable, the corrections can be avoided if the X-ray spectra are obtained from measurements of the intensity of emission of electrons accompanying the X-ray absorption process, suitably normalized to the "absorption jump" at the edge [17,18]. In this "total electron yield" detection method [24], the emission is one of the de-excitation processes responsible for filling the core level vacancies created by the absorption of the X-ray photons.

In a previous report from our laboratory on L_{III} and L_{II} X-ray absorption threshold resonances obtained by "total electron yield" measurements on a series of Ni–Cu alloys, it was concluded that the effect of the copper in decreasing the number of unfilled nickel d-states was an order of magnitude smaller than predicted by the rigid-band model [17]. To determine the applicability of this conclusion to other alloys of a Group VIII metal and a IB metal, we have extended the investigation to include the Pd–Ag and Pd–Au systems, both of which have been historically important in the exploration of the electronic factor in catalysis by metal alloys. Results for a series of Pd–Ag and Pd–Au alloys of different compositions are presented herein.

2. Experimental

The Pd–Ag and Pd–Au alloys were prepared by a method described by Kulifay [25]. An aqueous solution of ions of two metal elements is added to an aqueous solution of hydrazine dihydrochloride ($N_2H_4 \cdot 2HCl$) and ammonium hydroxide to bring about reduction of the ions and the formation of the alloy. The reduction step yielding the alloy is maintained at a temperature of 373 K for a period of approximately 1–1.5 h. The reagents used as sources of the metal elements in the present work were palladium nitrate, silver nitrate, and chloroauric acid. After the reduction step, the contents of the reaction flask were cooled to room temperature and the liquid was decanted from the solid metallic phase. The metal granules were then washed several times with hot water and subsequently dried overnight at a temperature of 383 K. Samples of pure Pd, Ag, and Au were prepared in the same manner by starting with solutions containing ions of only one metallic element.

The alloy samples used in the X-ray absorption studies were heated for an additional period of 4 h in a flow of nitrogen at a temperature of 1073 K to ensure homogeneity in the bulk. X-ray diffraction patterns on these samples exhibited very sharp lines. The dependence of the lattice parameter on alloy composition is shown in fig. 1 for both the Pd–Ag and Pd–Au alloys. In agreement with other published data on these systems [26,27], the lattice parameters of the alloys deviate very little from values given by a straight line joining the parameters of the pure metals; i.e., the data conform closely to Vegard's Law.

The X-ray absorption data were obtained at the Stanford Synchrotron Radiation Laboratory on beamline VI-2 using procedures developed for soft X-ray absorption spectroscopy. A Si(111) double crystal monochromator was used in the experiments. Measurements of total electron yields from the samples were made with a detector manufactured by Farrel Lytle (The EXAFS Company, Seattle, Washington). The yield is proportional to the extent of absorption of the X-rays. The samples used in the experiments consisted of finely divided granules of the alloys or pure metals mixed with powdered graphite and supported on Mylar tape. All absorption spectra were obtained at room temperature with the samples in contact with helium at atmospheric pressure. Because of a very small amount of argon impurity in the helium, the raw spectra of all of the palladium-containing samples exhibited an interference at an energy of 30 eV beyond the Pd L_{III} edge (argon K-edge absorption of photons from the incident X-ray beam). An argon K-edge spectrum was used in the data processing to account for the interference and thereby remove it from the spectrum of interest.

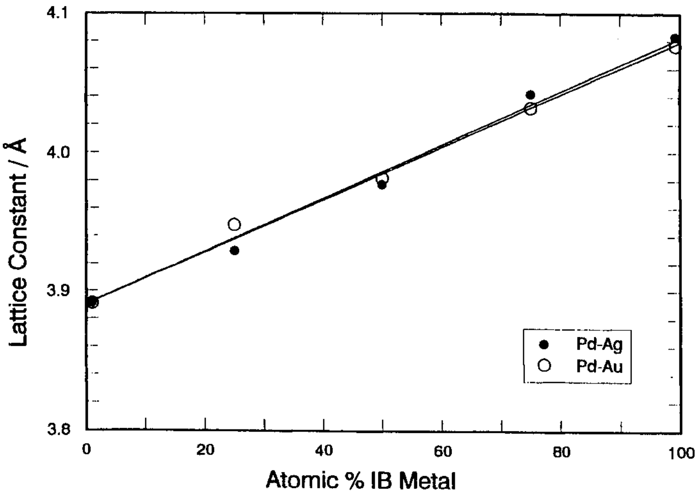

Fig. 1. Lattice constants of Pd–Ag and Pd–Au alloys as a function of composition: (●) Pd–Ag; (○) Pd–Au. The lines are least square lines through the data, the upper one for Pd–Ag and the lower one for Pd–Au.

3. Results

The processing of the X-ray absorption data at L_{III} and L_{II} edges involved the following procedure. In a raw spectrum (i.e., a plot of total electron yield versus X-ray energy), the pre-edge region of the spectrum was fitted by a straight line which was extrapolated forward to the energy corresponding to the point of inflection in the edge. The non-oscillatory component of the total electron yield in the post-edge region was fitted by a quadratic expression which was extrapolated back to this same energy. Over the range of energies fitted, the fitting parameters were such that the quadratic expression closely approximated a straight line parallel to the line fitted to the pre-edge region. The difference between the two extrapolated values of total electron yield (for the pre-edge and post-edge regions) is a measure of the increase in X-ray absorption characteristic of the edge. It is commonly known as the absorption jump, or step height. The spectrum in the region of the edge is normalized to this quantity. For the Pd–Ag alloys, the post-edge region of the spectrum for the palladium L_{II} edge is very short because of the close proximity of the silver L_{III} edge (the energy range between the two edges is only 20 eV). The following procedure was therefore adopted in the determination of the absorption jump at the palladium L_{II} edge. For the line fitting the non-oscillatory component of the electron yield in the post-edge region of the raw spectrum for pure palladium, we noted the energy at which the line intersects the initial rise in the spectrum immediately following the white line. The fitting line for a Pd–Ag alloy in the post-edge region was then constrained to intersect the analogous part of the spectrum at this same energy and to have a slope parallel to the fitting line for the pre-edge region.

An X-ray absorption spectrum for a Pd–Ag alloy containing 75% Pd (atomic percent) is shown in fig. 2. The spectrum includes all three of the L absorption

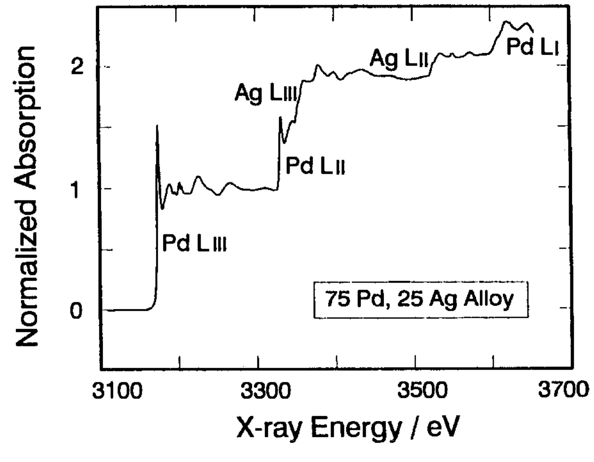

Fig. 2. X-ray absorption spectrum for a Pd–Ag alloy with a molar composition of 75% Pd, 25% Ag in the region of the L_{III} and L_{II} absorption edges of the two components, and including the L_I edge of palladium. The complete spectrum is normalized to the palladium L_{III} absorption jump.

edges of palladium, and the L_{III} and L_{II} edges of silver. The palladium edges exhibit absorption threshold resonances ("white lines"), whereas the silver edges do not. For this particular figure, the entire spectrum is normalized to the absorption jump at the palladium L_{III} edge. One can see that the composition of the Pd–Ag alloy is approximately reflected in the relative magnitudes of the L_{III} or L_{II} absorption jumps for the two components. This is not the case for the Pd–Au alloys, where the energy of an L edge of palladium differs greatly from the energy of the corresponding edge of gold.

In the measurement of total electron yields, it is well known that the depth of escape of electrons from the sample is limited. If the surface composition of an alloy differs substantially from the overall composition, one might then be concerned that the X-ray absorption data would not be representative of the latter. Since the relative magnitudes of the absorption jumps for the components of the Pd–Ag alloys are consistent with the overall compositions, we must conclude either that the surface composition is the same as the overall composition or that the escape depth of the electrons is significantly larger than the thickness of the surface region. For the Pd–Au alloys, we are not able to establish from X-ray absorption jumps alone that the data for these samples are representative of the overall compositions. However, it would seem to be reasonable to assume that the Pd–Au alloys are similar to the Pd–Ag alloys in this respect.

The normalized L_{III} and L_{II} absorption edges of pure silver are compared to the corresponding edges of pure palladium in the upper sections of fig. 3. The zero point in the energy scale is taken as the energy at which the point of inflection at the front of the palladium edge is observed. The edges for silver differ from those for palladium in not exhibiting pronounced peaks ("white lines") at the absorption thresholds. They have the appearances of simple steps and are due to excitations of electrons from 2p core levels of the silver atoms to continuum states external to the atoms. The more complex edges of palladium consist of similar step functions on which the resonance peaks are superimposed. When resolved from the step function at the edge, such a peak has Lorentzian line shape [28]. To resolve the Lorentzian function from the step function for pure palladium, we employ a method described by Lytle [29] with a modification suggested by Cordts et al. [26]. Since silver is the element immediately following palladium in the periodic table, the assumption is made that the step functions constituting the L_{III} and L_{II} edges of silver can be used to approximate the underlying step functions in the L_{III} and L_{II} edges of palladium. In the application of this method, the L_{III} or L_{II} edge of silver is shifted in energy to the region of the spectrum where the corresponding edge of palladium is observed. The energy corresponding to the point of inflection in the initial steeply rising part of the silver edge is aligned with the energy at which the maximum in the resonance peak of palladium is observed. This is done to achieve alignment of the components of the palladium edge at the energy corresponding to the Fermi energy [16]. The pre-edge region of the palladium edge from -25 to -7.5 eV is then fitted with the pre-edge region for the silver edge by a simple verti-

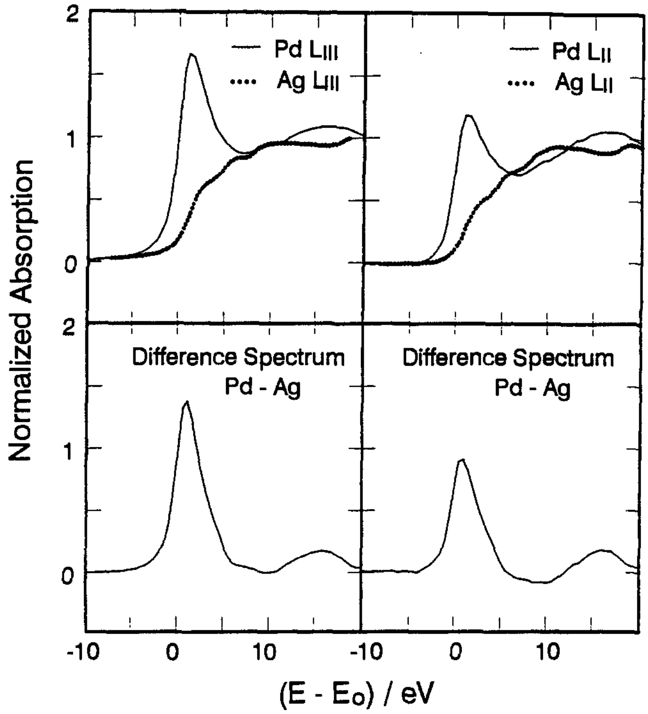

Fig. 3. Extraction of the spectral components representing the L_{III} and L_{II} absorption threshold resonances of palladium from the observed X-ray absorption spectrum of the pure metal, assuming that the L_{III} and L_{II} edges of silver can be substituted for the underlying step functions in the corresponding edges of palladium. In the upper two sections of the figure, the solid lines are the spectra for pure palladium while the dotted lines are the spectra for pure silver. Each of the silver edges is positioned so that the point of inflection in the initial steeply rising part of the edge is aligned with the maximum in the peak at the corresponding edge of palladium. The zero point in the energy scale is located at the point of inflection in the palladium edge. The difference spectra obtained by subtracting the broken lines from the solid lines are shown in the lower two sections of the figure. They are assumed to represent the L_{III} and L_{II} absorption threshold resonances of palladium

cal displacement of one spectrum relative to the other. In the post-edge regions the normalized absorptions for the palladium and silver are fitted to each other by applying a scaling factor (differing only slightly from unity) to one of the spectra. For the L_{III} post-edge regions, the fit was made over the energy range of 7.5–120 eV (referred to the zero point of the palladium L_{III} edge). The corresponding fitting range for the L_{II} post-edge regions was 7.5–18 eV (referred to the zero point of the L_{II} edge of palladium). The same L_{III} and L_{II} edge spectra for pure silver were fitted to the corresponding L_{III} and L_{II} spectra of palladium for samples of all compositions. The fitting procedure corrects for small differences introduced in the original normalizations of the spectra being compared.

Difference spectra obtained by subtracting the spectra for silver from those for palladium for both edges are shown in the lower sections of fig. 3. They approximate the absorption threshold resonances at the L_{III} and L_{II} edges of palladium. In a similar manner, we obtain the resonances for the palladium in Pd–Au or Pd–Ag alloys by subtracting the edges for pure silver from those for the palladium in the alloys, as illustrated in fig. 4. The resonances for the 25% Pd, 75% Au alloy and the 25% Pd, 75% Ag alloy are shown in the middle and lowest sections of fig. 4, respectively. For ease of comparison with the resonances for the alloys, the resonances for pure palladium from fig. 3 are shown again in the top section of fig. 4. The intensities of the resonances for the alloys are clearly lower than those for pure palladium. When similar data for the other alloys are also considered, we find that the intensities of the palladium resonances decrease with increasing content of the gold or silver in the alloy.

In continuing the analysis of the data, we note that the areas associated with the palladium L_{III} and L_{II} resonance lines have been determined by a procedure in which the X-ray absorption at an edge is normalized to the absorption jump at the same edge prior to subtraction of a similarly normalized absorption associated with transitions to the continuum. This procedure removes the effect of the different degeneracies of the $2p_{3/2}$ and $2p_{1/2}$ levels involved in the L_{III} and L_{II} resonances. A

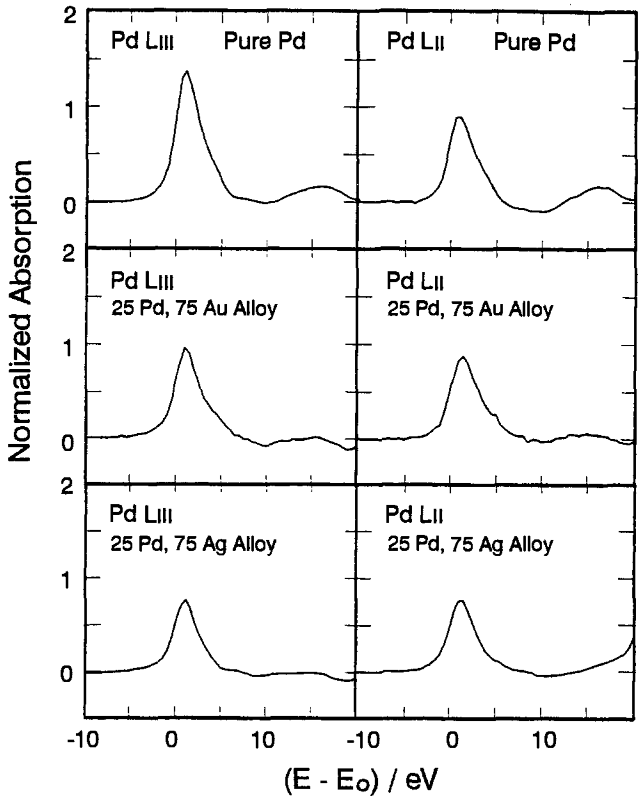

Fig. 4. Comparison of the absorption threshold resonances at the L_{III} and L_{II} edges of palladium with those at the corresponding edges of palladium in a 25% Pd, 75% Au alloy and in a 25% Pd, 75% Ag alloy.

measure of the number of unfilled palladium d-states is then given by the sum of the areas for the L_{III} and L_{II} resonances. This assumes that considerations of transition probabilities do not have a significant effect on the area of an L_{III} resonance line relative to the area of the corresponding L_{II} line. Normalization of the sum of the areas of the palladium L_{III} and L_{II} resonance lines for each alloy to the corresponding sum for palladium itself is thereby assumed to give the number of unfilled palladium d-states for the alloy relative to the number of pure palladium. Plots of this quantity for the Pd–Au and Pd–Ag alloys are shown as a function of alloy composition in fig. 5, along with a similar plot for Ni–Cu alloys taken from a previous paper from our group [17]. Also shown is a prediction for these systems based on the rigid band model of the electronic structure. The data for all three systems deviate substantially from the predicted effect, the most extreme deviation being that for the Ni–Cu system. However, there is a measurable effect of the Group IB metal on the number of unfilled d-states of the Group VIII metal for all three systems, the quantitative effect being greatest for the Pd–Ag alloys. The behavior of the Pd–Au system is intermediate to that of the Ni–Cu and Pd–Ag systems.

4. Discussion

The results of the X-ray absorption studies on Pd–Ag and Pd–Au alloys

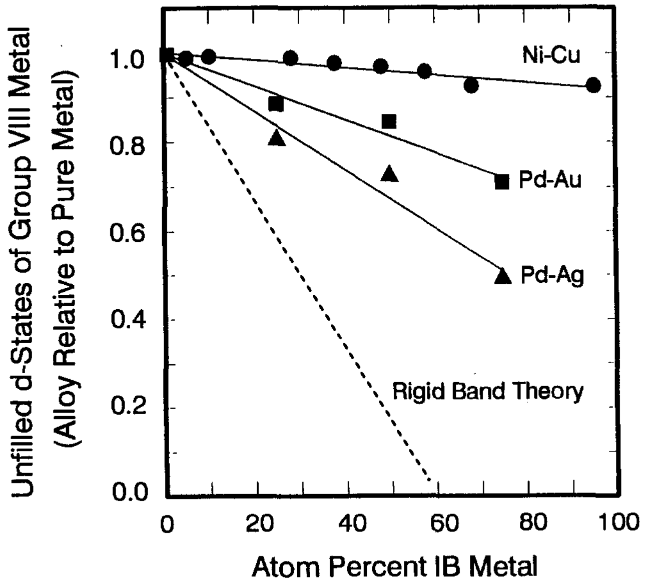

Fig. 5. Electronic structures of Ni–Cu, Pd–Au, and Pd– Ag alloys as a function of alloy composition. The ordinate represents the number of unfilled d-states per atom of Group VIII metal in the alloy relative to the number for the pure Group VIII metal. The solid lines and the data points were derived from X-ray absorption spectra. Data for Ni–Cu alloys are taken from a paper by Meitzner et al. [17]. For comparison, a prediction based on the rigid-band model of the electronic structure is shown as the broken line.

reported in this paper, and on Ni–Cu alloys in an earlier paper [17], lead to conclusions on the effect of alloy composition on electronic structure which differ from that predicted by the simple rigid-band model. The measured effects of the Group IB metals in decreasing the number of unoccupied d-states in the Group VIII metals are much smaller than predicted and are quantitatively different for the three alloy systems. The observation that the effect is much more pronounced for Pd–Ag than for Ni–Cu alloys is in accord with conclusions of Cordts et al. based on X-ray absorption coefficients derived from transmission experiments [15,16]. As mentioned earlier, the work of these investigators incorporated corrections for sample thickness effects. Consequently, the confirmation of their findings by results of experiments not requiring such corrections is gratifying. We reemphasize the important feature that X-ray absorption spectra derived from measurements of total electron yields are not complicated by sample thickness effects.

The extension of the X-ray absorption studies to a third system, Pd–Au, has revealed an effect of alloy composition on electronic structure which is larger than the effect found for Ni–Cu but smaller than that observed for Pd–Ag. In other words, the extent of chemical, or electronic, interaction between the components is quantitatively different for Ni–Cu, Pd–Au, and Pd–Ag alloys. According to the rigid-band model of the electronic structure, the three alloys should all exhibit the same relation between the number of vacant d-states and the atomic fraction of the IB metal present, namely, the relation indicated by the dotted line in fig. 5.

Although the results of the X-ray absorption studies on Ni–Cu, Pd–Au, and Pd–Ag alloys do not support the rigid-band model of electronic structure, they do provide a basis for relating catalytic observations to electronic (or ligand) effects [30]. In accordance with present-day views [31,32], such effects would be expected to be localized in nature, possibly involving only the interaction between nearest neighbor metal atoms rather than a collective effect of all of the atoms in a metal crystal or crystallite as a whole.

From the point of view of theories of the electronic structure of metal alloys, the rigid-band model represents one extreme, in which the same functional relation between the density of electronic states and energy is assumed for the alloys and pure metal components alike. According to this model, the only effect of the alloying is to change the Fermi level. The model has the feature that the outermost shells of d and s electrons of the component atoms are redistributed equally among the two types of atomic sites in an alloy, so that the sites have substantial ionic character. Another extreme is represented by the "minimum polarity model" [12], in which an atom in an alloy has the same electronic configuration as it has in the pure metal. Consequently, the atomic sites in an alloy remain neutral in the alternative model. The results of the present work indicate that the true state of affairs lies somewhere between the extremes represented by the two models, and depends in detail upon the particular alloy system involved.

Acknowledgement

The authors are grateful to Mr. William J. Mykytka for the preparation of the Pd–Ag and Pd–Au alloys and to Dr. Baoshan Zhang for X-ray diffraction measurements on the alloys.

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