X-ray photoemission and Auger energy shifts in some gold-palladium alloys

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We report the results of x-ray photoemission (XPS) and Auger electron spectroscopies in the alloy Au_xPd_{1-x} for various concentrations. By comparing the predictions of the excited-atom version of the quasiatomic model with the dilute Au results, we show that charge-transfer corrections to the Au Auger kinetic-energy shift, $\Delta\varepsilon_{ijk}^{Au}$, are small. This result supports the validity of the relation $\Delta\varepsilon_{ijk}^{Au} \simeq -\Delta E_F^{Au} \equiv E_F^{Au} - E_F(x)$ [where E_F^{Au} and $E_F(x)$ are the Fermi energies in pure Au and the alloy, respectively] and permits determination of the order of magnitude of the charge transfer from Auger measurements alone (i.e., hundredths of electrons/atom). Such small charge transfer seems to hold also for the Ag and Cu atoms in Pd-Ag, Au-Ag, Pd-Cu, and Au-Cu. Furthermore, these results are consistent with interpretation of the Au Auger parameter shift, $\Delta\xi^{Au}$, as well as with analysis of $\Delta\omega^{Au}$, the valence-electron contribution to the Au XPS core binding energy; we predict that $\Delta\xi \simeq \Delta\omega$ for noble metals in general. This analysis yields the result that the dilute Au d-valence-electron occupations change $\simeq -0.2$ electrons/atom, approximately the negative of the sp change from isomer shifts. The Pd results are consistent with small charge transfer and a small gain of d electrons.

I. INTRODUCTION

One of the principal problems in the study of the electronic structure of metallic alloys is that of determining the charge transferred between the component atoms upon formation of an alloy. A number of x-ray photoemission spectroscopy (XPS) studies have been addressed to this and the related problem of measuring the changes in electron distribution among the valence states of an atom.[1-9] An experimental quantity used in determining electronic occupation changes of species A in the alloy A_xB_{1-x} (where x is the concentration of A) is the core-level binding energy shift, $\Delta B^A(x)$, relative to pure metallic A, which is usually expressed as

$$\Delta B^A(x) = \Delta E_F^A(x) - \Delta\omega^A(x) , \tag{1a}$$

$$\Delta E_F^A(x) \equiv E_F(x) - E_F^A . \tag{1b}$$

The quantities $E_F(x)$ and E_F^A are the Fermi energies in the alloy and pure A, respectively, and $\omega^A(x)$ denotes the A-atom valence-electron contribution to the binding energy of species A. In order to characterize the bulk electronic structure independent of surface conditions, $E_F(x)$ and $\omega^A(x)$ are both defined with respect to a *bulk* energy zero[10] [in jellium, for example, $E_F(x)$ is the difference between the surface dipole barrier and the work function].[10] With this definition, $E_F(x)$ is probably unmeasurable directly. Although the *relative* Fermi energy $\Delta E_F^A(x)$ presents no such fundamental difficulties, its specification has been hardly trivial. One method has been that of replacing $\Delta E_F^A(x)$ by $\phi^A - \phi(x)$,[1-4] where ϕ^A is the work function of pure A and $\phi(x)$ that of the alloy, thereby neglecting dipole-barrier and surface effects.

The quasiatomic model (QAM) of screening of excited states describes a large body of x-ray-excited Auger spectroscopy (XAES) and XPS data.[10-12] A prediction[10-12] based on this model is that, if A is a noble metal in A_xB_{1-x}, then $\Delta\varepsilon_{ijk}^A(x) \cong -\Delta E_F^A(x)$, where $\Delta\varepsilon_{ijk}^A$ is the XAES shift with respect to pure A (we henceforth suppress i, j, and k, which denote core levels of A). This prediction is strictly valid[10-12] only if volume change and charge-transfer effects are negligible. The consistency of the consequences of this hypothesis with the results of previous, independent, XPS studies has been reported.[10-12]

The relation between the XAES shift and the relative Fermi energy changes when we consider volume change and charge transfer. In fact, it can be shown[13] that the excited-atom version[14,15] of the QAM predicts the following relation for the XAES shift, $\Delta\varepsilon^A$, if A is a pure noble metal:

$$\Delta\varepsilon^A(x) = -\Delta E_F^A(x) + \Delta_v(x) + \Delta_c(x) , \tag{2}$$

where Δ_v and Δ_c involve, respectively, atomic volume and charge-transfer changes induced by alloying. In deriving Eq. (2), we assume that, in the alloy and the pure metal, the noble-metal ground-state d density of states (DOS) has less than one hole and that the screening electrons self-consistently occupy the lowest available atomic valence shell.[13] Consequently, the fully screened initial (i.e., one core hole) and final (i.e., two core holes) noble-metal states involved in the Auger process correspond to full local d DOS (i.e., of z^A+1 and z^A+2 atoms, respectively, where z^A is the atomic number of A).

Only the first term on the right in Eq. (2) is transitive and then only the dilute A limit: that is, $E_F^B - E_F^A = E_F^B - E_F^C - (E_F^A - E_F^C)$. A necessary condition for the validity of the hypothesis $\Delta\varepsilon^A(x) \cong -\Delta E_F^A(x)$ is,

therefore, that the Auger-energy shifts in the corresponding dilute alloys obey this transitive relation; it should be noted that the Auger shifts of different noble-metal atoms in different alloys must be involved in testing the transitivity. A corollary is that transitivity of the Auger-energy shifts implies that volume and charge-transfer effects are small. The transitivity of this relation was verified[10−12] in the alloy pairs (Au-Ag, Au-Cu) and (Pd-Cu, Pd-Ag). In all the alloys we study, $V(x) = xV_A + (1-x)V_B$ to a good approximation [where $V(x)$ is the alloy lattice volume and V_A is the atomic volume in the metal A], so that we would expect volume effects to be small. That Δ_c, which has the form of the total electron occupation change of A (or, the charge transfer) times a conduction-state Coulomb integral (whose order is 1 Ry),[13] is small (that is, no larger than the experimental error, or 0.15 eV), implies a very small value for the magnitude of the charge transfer in these alloys (of the order of hundredths of electrons/atom). This conclusion is based solely on Auger measurements and supported by XPS studies of Pt-Cu (Ref. 7) and Pd-Cu.[8]

In this paper we combine XAES and XPS data to test this hypothesis in the alloy Pd-Au which was chosen for this work for the following reasons: (a) In previous studies of Pt-Cu (Refs. 5–7) and Pd-Cu,[8,9] as well as in other transition-metal–noble-metal alloys,[1−4] little if any charge transfer was found, so that comparison with Pd-Au would be interesting: (b) Pd-Au is, as are Pd-Cu and Pt-Cu, an almost ideal solid solution across the entire concentration range; (c) since Au has a wide d band, and Cu a narrow one, comparison of Pd-Au and Pd-Cu may clarify the role of d-band width in charge transfer; (d) Au is the most electronegative noble metal and Mössbauer studies of Pd-Au (Ref. 3) have shown an increase in the Au s-state occupation, so that one might expect sizable charge transfer in this system; (e) finally, there is considerable interest in its catalytic properties.[16−18]

This paper is organized into four sections. In Sec. II we describe the experimental techniques employed and the measured results. Section III comprises a discussion of these results, where we show first that the dilute Cu and Ag XAES energy shifts, respectively, in the alloy pairs (Pd-Cu, Au-Cu) and (Pd-Ag, Au-Ag) and that of dilute Au in Pd-Au obey transitive relations (within experimental error), in support of the identification of relative Fermi energies with the negative of the noble-metal Auger core-level shifts.[10−12] Such identification in Pd-Au is consistent with those reported for other alloy systems.[10−12] A by-product of this relation is the immediate conclusion, *from Auger measurements alone*, that the magnitude of the charge transferred to Au is small in the dilute alloy (of the order of hundredths of electrons/atom). Application of these relative Fermi energies to XPS core-level shifts permits us to isolate the valence contribution to the binding-energy shift, which, in noble metals, is approximately equal to the Auger parameter shift. In particular, combination of the XAES energy shifts with the results of isomer-shift measurements[3] in the dilute Au regime allows us to derive the charge transferred to Au from the XPS binding-energy shifts: the resulting values are consistent with those derived from the XAES measurements. Finally, we present our conclusions in Sec. IV.

II. EXPERIMENTAL RESULTS

The alloy samples studied were prepared from stoichiometric quantities of the constituent metals, which were melted in an arc furnace in argon atmosphere, then plastically deformed after homogenization at 1000 °C for 4 days, and finally rolled into thin foils (approximately
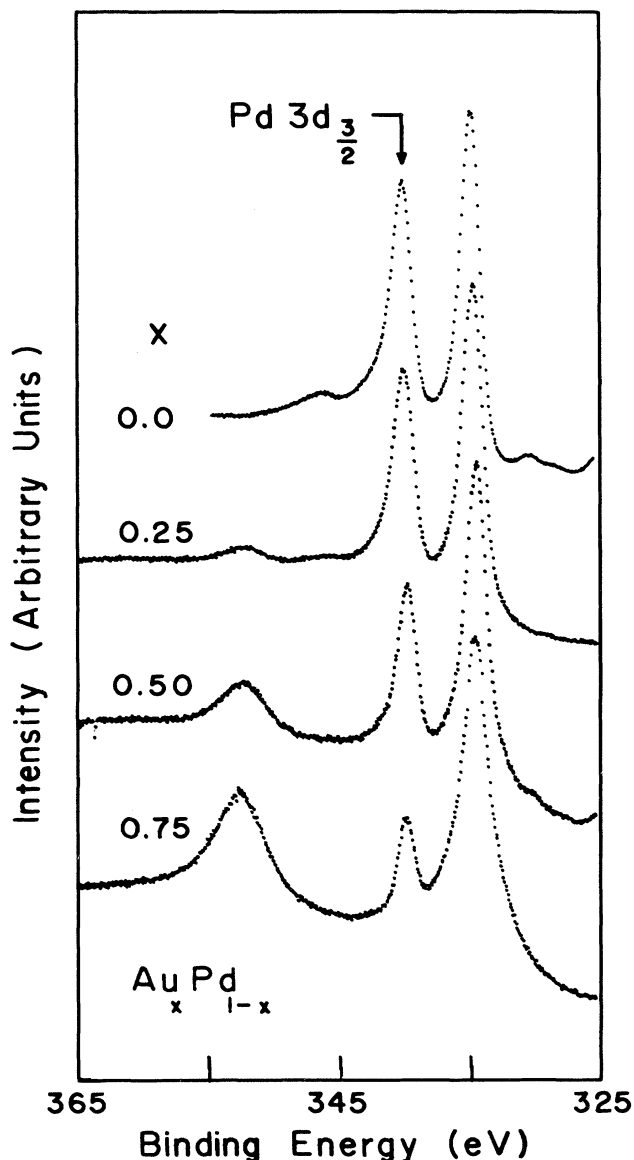

FIG. 1. Typical XPS Pd $3d$ spectra in Au_xPd_{1-x}, where x corresponds to the Au concentration. The peaks located around 335 eV result from the overlap of the Pd $3d_{5/2}$ and Au $4d_{5/2}$ lines. The peak around 353 eV corresponds to the Au $4d_{3/2}$ line. Pd binding-energy shifts are extracted from the Pd $3d_{3/2}$ lines.

0.2 mm thickness and 10 cm^2 area). The nominal bulk composition of the samples was determined from electron microprobe analysis (0.01 error). Diffractometer measurements showed that the samples were polycrystalline, with small negative deviations (i.e., $\sim 0.5\%$) of the lattice constant from Vegard's law.[19]

The Pd and Au XPS measurements were performed using Al $K\alpha$ radiation (1486.6 eV) with a McPherson ESCA-36 (background pressure of around 10^{-8} Torr) and

a Vacuum Science Workshop (VSW) Ha 100 (10^{-9}–10^{-10} Torr) spectrometer, respectively. The samples were cleaned by argon-ion sputtering, with subsequent heating for a few minutes at temperatures between 500 °C and 800 °C to remove sputter damage.[8] Contamination of the alloys was monitored through the carbon $1s$ line (285 eV).

The McPherson spectrometer is an electrostatic analyzer without retarding optics and yielded a Au $4f_{7/2}$ full width at half maximum (FWHM) of around 1.0 eV. The VSW spectrometer was operated in fixed analyzer transmission (FAT) mode with a pass energy of 44 eV (FWHM of 1.5 eV for the Au $4f_{7/2}$) and the insensitivity of the energy centroid shifts to the FAT mode was verified. The two spectrometers were calibrated with respect to the Au $4f_{7/2}$ line (i.e., 84.0 eV) and measured binding energies were reproducible to within ± 0.1 eV, so that the shifts reported here are accurate to within ± 0.15 eV and the differences in shifts (i.e., the $\Delta\omega$) to within ± 0.2 eV.

In Figs. 1 and 2 we present the Pd $3d$ and Au $4f$ lines, respectively, for the various concentrations studied. The peaks located at around 335 eV in Fig. 1 result from the overlap of the Pd $3d_{5/2}$ and Au $4d_{5/2}$ lines, obliging us to measure the less intense Pd $3d_{3/2}$ as well as the Au $4f_{7/2}$ lines in our binding-energy shift studies. The corresponding Au and Pd XPS binding-energy shifts are represented by squares in Figs. 3 and 4, respectively. It is interesting to note they are negative for both Pd and Au, in contrast to Pd-Cu,[8,20] where the Pd shifts are positive and the Cu negative.
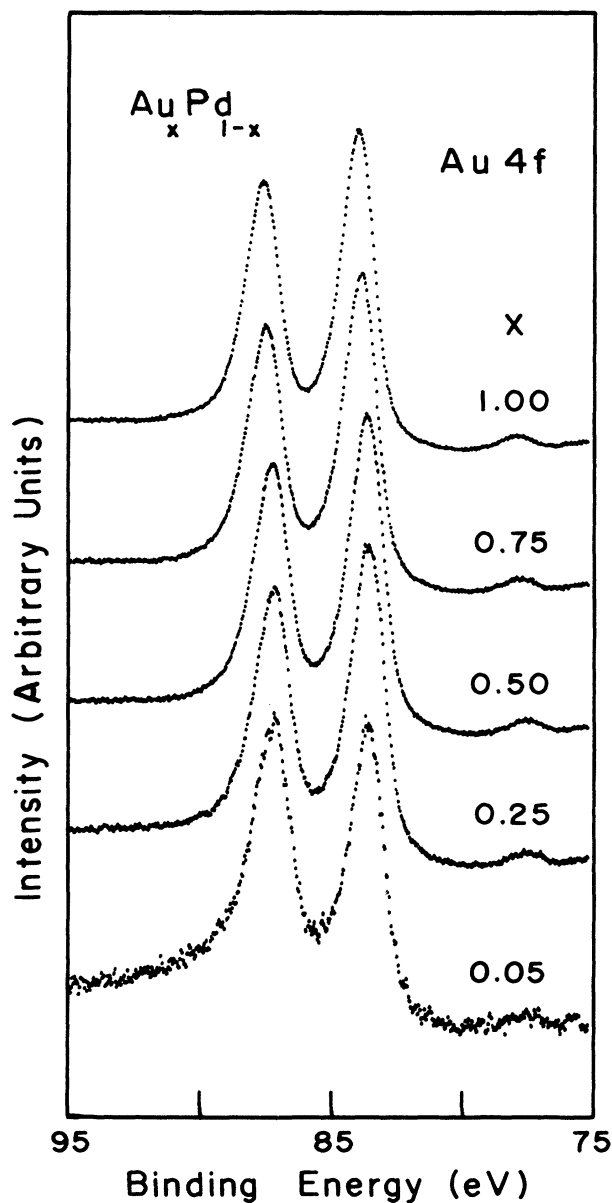

FIG. 2. Typical XPS Au $4f$ spectra in Au$_x$Pd$_{1-x}$. The change in relative intensities at $x = 0.05$ result from the overlap of the Au $4f_{5/2}$ and the weak Pd $4s$ lines. Au binding-energy shifts are measured for the Au $4f_{7/2}$ lines.
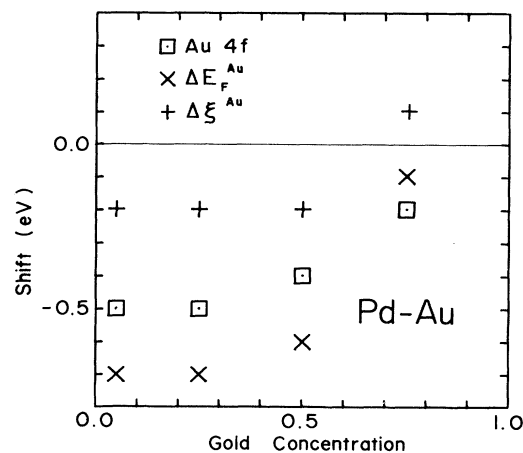

FIG. 3. Au energy shifts in Au$_x$Pd$_{1-x}$. The squares correspond to ΔB^{Au}, the Au XPS binding energy shifts; the crosses represent $-\Delta\varepsilon^{\text{Au}}$, the negatives of the Au $M_{4,5}N_6N_6$ XAES kinetic-energy shifts, which we identify in the text with the relative Fermi energies, ΔE_F^{Au}; and the pluses symbolize the Au Auger parameter shifts, $\Delta\xi^{\text{Au}} \equiv -\Delta\varepsilon^{\text{Au}} - \Delta B^{\text{Au}}$, which we identify with $\Delta\omega^{\text{Au}}$, the Au valence-electron contribution to the XPS shift. Utilization of previous Au isomer-shift results yields very small Au charge transfers. Note the nonlinearity of the XAES shifts for $x \sim 0.5$.
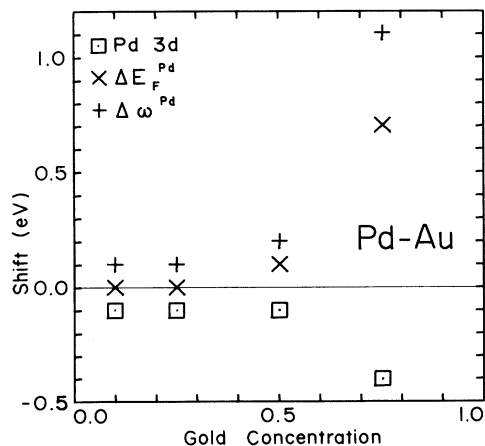
FIG. 4. Pd energy shifts in Au_xPd_{1-x}. The squares represent ΔB^{Pd}, the Pd XPS binding-energy shifts; the crosses denote $\Delta E_F^{Pd}(x) \equiv \Delta E_F^{Au}(x) - (E_F^{Pd} - E_F^{Au}) \cong -\Delta\varepsilon^{Au}(x) + 0.7$ eV, as described in the text; and the pluses correspond to $\Delta\omega^{Pd} \equiv \Delta E_F^{Pd} - \Delta B^{Pd}$, which we identify with the Pd valence-electron contribution to ΔB^{Pd}. Note that, although the Au and Pd XPS shifts are both negative, the respective values of $\Delta\omega$ have different signs. The Pd results seem to be consistent with very small charge transfer and a gain of d electrons.

In order to test the hypothesis that the XAES noble-metal shifts can be used to extract the relative Fermi energies in the alloy, we measured the Au $M_{4,5}N_6N_6$ spectra with our VSW analyzer by bremsstrahlung excited Auger spectroscopy (BEAS).[21-23] The negatives of the resulting Auger energy shifts for Au_xPd_{1-x} are represented by crosses in Fig. 3.

III. DISCUSSION

Investigation of ground-state valence-electronic structure in pure transition and noble metals and their alloys by means of XPS and of theoretical calculations has been the subject of a great many reports. Many workers[1-4,24-32] have concluded that charge transfer of the d electrons to the noble-metal atoms in these alloys is small and overcompensated by the s- and p-electron transfer (suggestions[33,34] that Au-Zn and Au-Mg exhibit significant charge transfer should be noted). In particular, such XPS data as valence-band, satellite, core-level spectra,[29] and core-level binding-energy shifts[1-4,7,8] have all been used to reach conclusions regarding changes in the local densities of states of the components with respect to those of the corresponding pure metals. It is important to note that most of the above-mentioned measurements[24-32] give information only about the local DOS near the Fermi level. Only the core-level binding-energy shift measurements directly involve changes in valence-band occupations, or integrals of the local DOS. Previous analyses, which used Mössbauer isomer shifts,[1-4,33] relied upon work-function data to derive rel-

ative Fermi energies.

It is desirable, therefore, to formulate a method which directly extracts valence-electron occupation changes from core-level binding-energy shifts while minimizing the Fermi-energy-related ambiguities mentioned above. Such a method for alloy A_xB_{1-x}, where A is a noble metal, was proposed[10-12] to be based on the identification of the noble-metal A XAES shift, $\Delta\varepsilon^A(x)$, with the negative of the relative Fermi energy, $-\Delta E_F^A(x)$ [i.e., see Eq. (2)]. Validity of this relation requires that the volume change and charge-transfer corrections in Eq. (2) be small. In other words, it is necessary that the dilute noble-metal XAES shifts obey a transitive relation, as discussed in Sec. I.

With the definition $F(B-A) \equiv -\Delta\varepsilon^A(0)$ (i.e., the dilution limit of noble metal A in A_xB_{1-x}), transitivity is obeyed when $F(C-B) = F(C-A) - F(B-A)$: that is, independent of A. F(Pd-Ag) and F(Au-Ag) previously reported[10] were -0.6, and 0.0 eV, respectively, whereas F(Pd-Cu) and F(Au-Cu) were -0.4 and 0.3 eV, respectively. For the (Pd-Ag, Au-Ag) and (Pd-Cu, Au-Cu) alloy pairs we have, therefore, -0.6 and -0.7 eV, respectively, for F(Pd-Ag) $- F$(Au-Ag) and F(Pd-Cu) $- F$(Au-Cu), which compare favorably with the value of -0.7 eV from Fig. 3 for the dilute Au limit in Pd-Au, or F(Pd-Au). It would seem, therefore, that, in these dilute alloys, the XAES energy shifts obey a transitive relation *even when the Auger shifts involved are measured for different noble-metal atoms*, lending support to the relation $\Delta E_F^A \cong -\Delta\varepsilon^A$, as discussed above.

Deviation from transitivity is produced by volume and charge-transfer effects, as in Eq. (2). Since we expect the first of these to be small in all these alloys, the transitivity of the Auger shifts which we observe indicates that the order of magnitude of the effects of possible charge transfer to the noble-metal atoms is within our experimental error, or 0.15 eV. According to the excited-atom version of the QAM,[14,15] in which the screening electrons self-consistently occupy the lowest available atomic valence shell, it follows[13] that the charge-transfer contribution to the noble-metal XAES shift is of the form of a Coulomb integral (of the order of rydbergs) times the charge transfer. We expect therefore, the magnitude of the charge transfer to the noble-metal atoms in all these alloys (including Pd-Au) to be on the order of 0.01 electron/atom.

From our study of the transitivity of the XAES shifts in the dilute Au limit, we conclude that the volume (Δ_v) and charge-transfer (Δ_c) terms in Eq. (2) are small. Since we expect these terms to take their largest values in this limit, their contribution should be even less at intermediate compositions. The identification of the Au XAES shifts with the relative Fermi energies appears, therefore, to be justified at intermediate concentrations as well. In Fig. 3 we illustrate $-\Delta\varepsilon^{Au}(x) \simeq \Delta E_F^{Au}(x)$, and in Fig. 4 the related quantity $\Delta E_F^{Pd}(x) = E_F(x) - E_F^{Au} - (E_F^{Pd} - E_F^{Au}) \simeq -\Delta\varepsilon^{Au}(x) - F(Pd-Au) = 0.7 -\Delta\varepsilon^{Au}(x)$, where x is the Au concentration. It is interesting to note that, although the absolute values of the relative Fermi energies derived in this way tend to decrease with increasing x, they are not linear and, indeed,

there appears to be an abrupt change in their magnitudes in the vicinity of $x \sim 0.5$. For lower concentrations, the variation is slow. This nonlinear behavior is manifested in other alloys as well,[13] and contrasts with extrapolations of work-function measurements.[35] For example, work-function differences employed previously[3] (i.e., -0.2 ± 0.2 eV) are different from the values of ΔE_F^{Au} presented in Fig. 3. Obviously, use of the correct Fermi-energy contribution is important.

These results, derived from Auger measurements alone, are, of course, meaningful only if they are consistent with the XPS data. For most metals, $\Delta\omega^A$ in Eq. (1a) can be approximated[1-4] as

$$\Delta\omega^A \cong U_d^A \delta^A - (U_d^A - U_c^A)\delta n_c^A ,$$ (3)

where δn_i^A and U_i^A represent the occupation number change upon alloying and the effective Coulomb integral, respectively, of the ith valence electrons of atom A (i.e., $i=c$ for sp and $i=d$ for d valence electrons), $\delta^A \equiv \delta n_d^A + \delta n_c^A$ is the charge transfer to atom A, and we suppress the concentration dependence.

It is important to recognize that, in Eq. (1), valence-electron occupation changes associated with excited atom A are included in the $\Delta\omega^A$ term; these changes include those produced by screening of core holes. All other valence-electron charge-density contributions (even those associated with Madelung terms[1-4]) are incorporated in the ΔE_F^A term.[10]

When we consider noble metals, for which the nature of the core-hole screening changes from d -to s-like,[22,23,36] we must modify the expression for $\Delta\omega^A$. That is, neglecting volume corrections and the core-hole occupation dependence of the U's, we have, for noble metals,[13]

$$\Delta\omega^A \cong W_d^A \delta^A - (W_d^A - U_c^A)\delta n_c^A ,$$ (4a)

$$W_d^A \equiv (U_d^A - U_c^A)p^A + U_c^A ,$$ (4b)

where p^A represents the number of d-valence band holes/atom in pure A. Note that, as a consequence of the screening, the d-electron contribution in Eq. (4) is diminished relative to that in Eq. (3); a more complete expression is presented elsewhere.[13] Values of $\Delta\omega^{Au}$ derived from Eq. (1a) by assuming $\Delta E_F^A \cong -\Delta\varepsilon^A$ are represented by pluses in Fig. 3.

Isomer-shift measurements in the dilute Au limit[3] in Pd-Au indicate a Au conduction-electron change of around 0.2 electron/atom. Substituting the dilute Au value of $\Delta\omega^{Au}$ from Fig. 3, previously reported[35] values for U_d^{Au} (i.e., 1.19 Ry) and U_c^{Au} (i.e., 0.95 Ry), and $p^{Au}=0.4$, we derive a total charge transfer of 0.00 electron/atom for Au (taking the range of experimental error into account yields $0.02 \geq \delta^{Au} \geq -0.01$ electron/atom for dilute Au concentrations). The striking agreement with the magnitudes derived solely from the Auger shift measurements is not necessarily meaningful because of the various uncertainties involved (e.g., the isomer shifts[3] were measured for samples different from ours). The exact values derived seem to be less important than the prediction, by both methods, that the magnitude

of the charge transfer is very small.

Application of the previous analysis to intermediate concentrations yields the result that $0.0 \geq \Delta\omega^{Au} \geq -0.2$ eV for $x \leq 0.5$, as represented by pluses in Fig. 3. When we take into account the dilute Au results, the picture which emerges is that the charge transferred to Au is very small in this alloy system so that the d and sp occupation changes basically compensate one another.[3] From the dilute Au isomer-shift results,[3] we expect the Au conduction-electron change to be positive and no more than 0.2 electrons. We feel that the small positive value of $\Delta\omega^{Au}$ for $x=0.75$ (i.e., 0.1 eV) is a consequence of uncertainties in our measurements, as we discuss below in terms of Auger parameter shifts.

Our experimental determination of the valence contribution to the noble-metal XPS binding energy involves setting $\Delta\omega^{Au}(x)$ in Eq. (1a) equal to $-\Delta\varepsilon^{Au}(x) - \Delta B^{Au}(x)$, which is precisely the experimental definition[36,37] of the Auger parameter shift, $\Delta\xi^{Au}(x)$; it is well to note that this relation between $\Delta\omega(x)$ and $\Delta\xi(x)$ holds only for noble metals. Exploitation of this relation permits us to gain insight into the mechanisms involved and the validity of our assumptions, as we discuss below.

In pure transition metals, the Auger parameter ξ is a measure of the strength of the interaction between the two final-state holes and is determined by the efficacy of screening by the ground-state d-band holes[22,23,36] [we denote the species A Auger parameter in pure metal A as ξ^A and that in the alloy as $\xi^A(x)$]. For example, the relatively large number of d-band holes in Pt screen the final-state core holes efficiently and, so, reduce ξ^{Pt} relative to ξ^{Au} because of the paucity of d-band holes in Au (Refs. 22 and 23)] relative to Pt; similar arguments apply to the $3d$-transition-metal series.[36] That ξ^{Au} is large [i.e., $\xi^{Au}=16.7$ eV (Ref. 23)] lends support to the validity of the excited-atom version of the QAM,[14,15] the assumptions of which underlie our basic relation: $\Delta\varepsilon^A(x) \cong -\Delta E_F^A(x)$.

The small absolute values of the $\Delta\xi^{Au}(x)$ in Fig. 3 lead us to conclude that $\xi^{Au}(x)$ is approximately equal to its value in pure Au for all concentrations measured, implying that the excited-atom version of the QAM (Refs. 14 and 15) is valid and that the ground-state valence-electron configuration is similar (i.e., there is less than one Au d hole) in the alloy as well: these conclusions support the assumptions we use to derive Eq. (2).[13] In addition, the small negative value of $\Delta\xi^{Au}(x)$ in the dilute Au limit implies a small increase in the number of d holes in the ground-state local DOS of neutral Au, in accord with our conclusion, based upon isomer-shift measurements[3] and Eqs. (4), that δn_d^{Au} is small and negative. Finally, the significance of $\Delta\xi^{Au}(x)$ in terms of the initial number of ground-state d holes indicates that its magnitude should not increase as we increase x, lending support to our analyses of intermediate compositions; furthermore, this interpretation indicates that the sign change at higher compositions is probably an artifact of experimental uncertainties.

From our discussion of $\Delta\omega^{Au}$ as an Auger parameter shift, it becomes clear that the smallness of the measured values is an unavoidable consequence of the validity of

the model we use to interpret the data. It is inconvenient that, in the case of Au in Pd-Au, the magnitude of the data is of the same order as the uncertainties in their determination, but, from this point of view, not necessarily surprising.

Similar analysis of the Pd binding energies is straightforward and the results for $\Delta\omega^{Pd}$ are manifested in Fig. 4. Although both the Au and Pd binding energies are uniformly negative, it is interesting that, throughout most of the concentration range, the corresponding values of $\Delta\omega$ have different signs. Determination of limits for the valence-electron occupation changes is more complicated in this situation, where isomer-shift measurements are not available. We can, however, make some progress by considering $x = 0.5$, where, by charge neutrality, the Pd and Au charge transfers are equal in magnitude and opposite in sign. Assuming the negatives of the extremes of the Au charge transfer calculated in the dilute Au limit as upper and lower limits on the charge transfer to the Pd, we derive $0.0 \geq \delta n_c^{Pd} \geq -0.2$ electrons/atom (this result takes into account the range of error in the values of $\Delta\omega^{Pd}$). Analysis of the Pd valence occupation changes at lower Pd concentrations is more difficult because of the uncertainties and the ill-conditioned nature of Eq. (2).[1-4] Nevertheless, the derived values of $\Delta\omega^{Pd}$ seem to be consistent with little charge transferred to the Pd and a small net loss of valence-conduction electrons (net gain of d electrons), as opposed to the case of Au, which appears to have a net gain of valence-conduction electrons.

That Au gains sp and loses an almost compensating number of d electrons is in agreement with previous experimental results[1-4] and calculations[30-32] on other alloy systems. The very small amount of charge transfer (i.e., hundredths of electrons/atom) is somewhat surprising, however.

XPS (Ref. 33) and Auger parameter[34] studies of 50% Au-Zr and Au-Mg alloys adduced significant charge transfer in those systems. Although charge-transfer effects would modify some of our arguments (in particular, those involving the significance of the Auger parameter shifts), they are negligible in Au-Pd and we postpone critical discussion of them to another publication.[13]

Another point involves the relative contributions of the Fermi energy and valence occupation changes to the initial-state core-level binding-energy shift (denoted as Δb_i^{Au}). In calculations[30] of most Au-$5d$ alloys, the d-count change contribution seems to dominate; this appears not to be the case for Au-Pt and Au-Ir.[30] We can estimate this shift for dilute Au from Eqs. (1) and (3) with the same values of U_i^{Au} as in our analysis of Eqs. (4). The result is $-1.0 \geq \Delta b_i^{Au} \geq -1.5$ eV for $0.02 \geq \delta^{Au} \geq -0.01$ electrons/atom. Consequently, the Fermi-energy change makes an important contribution and Δb_i^{Au} seems not to be dominated by changing local d count, in agreement with the Au-Pt calculations,[30] although the magnitudes of our estimates are much larger than those calculated. The difference in magnitude between our values of ΔB^{Au} and Δb_i^{Au} emphasizes the importance of final-state effects as embodied in the parameter p^{Au} in Eq. (4) in this simple model. A more complete expression is given elsewhere.[13]

Recent extended x-ray-absorption fine-structure

(EXAFS) experiments[38] in dilute Pd alloys indicate a local distortion of the lattice around the Pd atom in Pd-Cu but not in Pd-Ag. This distortion was invoked[38] to explain previous discrepancies in analyses of Pd MNN line shapes in Pd-Cu in terms of valence-band DOS modifications. Our derivation[10] of Eqs. (1) attributes all local screening electron density changes to the $\Delta\omega^A$ term, in accordance with the excited-atom version of the QAM.[14,15] All other electron density changes outside this local volume are incorporated in the ΔE_F^A term.[10] In a random alloy with no local lattice distortion, therefore, the site-dependent terms are included in the $\Delta\omega^A$ term and the definition of ΔE_F^A is consistent with the notion of relative Fermi energy. Should there be such a distortion around the noble-metal atom, as for Pd in the Pd-Cu experiments,[38] ΔE_F^A would be site dependent and its interpretation as a relative Fermi energy invalidated. We would not expect such site-dependent terms to exhibit the sort of transitivity we observe here, however, so that such contributions would not seem to be important for the Au and other noble-metal[10-12] results. The situation of Pd in Pd-Au is much less clear and we have no assurance that local lattice distortion is unimportant. Investigation of Pd XAES spectra should elucidate this issue.

IV. CONCLUSIONS

In this paper we investigate the validity of the relation $\Delta\varepsilon^A(x) \cong -\Delta E_F^A(x)$ and its consequences in Pd-Au and reach the following conclusions.

(a) Validity of the identification of $-\Delta\varepsilon^A(x)$ with $\Delta E_F^A(x)$ for noble metal A implies that the dilute Au XAES shift must be equal to the difference between the dilute Ag XAES shifts in Pd-Ag and Au-Ag as well as the difference between the dilute Cu XAES shifts in Pd-Cu and Au-Cu: in other words, verification requires measurements of different noble-metal Auger shifts in different dilute alloys. In Sec. III we show that these equalities do indeed hold, within experimental error, which emphasizes the transitive nature of the dilute noble-metal XAES shift.

(b) A corollary of the transitivity of the dilute Au shift is that the volume and charge-transfer corrections in Eq. (2) are of the order of the experimental error (i.e., 0.15 eV). Since we expect the first of these corrections to be small, we deduce immediatly from Auger measurements alone that the charge-transfer correction alone is on the order of the experimental error, implying a charge transfer to the Au whose magnitude is on the order of hundredths of electrons/atom. Since transitivity is obeyed in the other dilute alloys used to test the identification of Auger shift and relative Fermi energy, these corrections appear to be small in these dilute alloys as well, leading to charge transfers to their noble-metal atoms of the same order as in dilute Pd-Au.

(c) We expect the volume and charge-transfer corrections in Eq. (2) to take their largest values in the dilute Au limit, implying that their contribution is even smaller at intermediate concentrations, so that the relationship between the XAES shift and the relative Fermi energy established in the dilute limit should be valid at these con-

centrations as well; similar arguments are applicable to the other alloys involved in testing the transitivity, as was reported previously.[10-12] Derivation of ΔE_F^{Pd}, the Fermi energy relative to that in pure Pd, is immediate and Figs. 3 and 4 display $\Delta E_F^{Au}(x)$ and $\Delta E_F^{Pd}(x)$, respectively.

(d) Application of the results for the relative Fermi energies permits us to isolate $\Delta \omega^A(x)$, the contribution of the valence electrons to the XPS binding-energy shifts, $\Delta B^A(x)$ [i.e., $\Delta \omega^A(x) \equiv \Delta E_F^A(x) - \Delta B^A(x)$]. It is interesting that, although both $\Delta B^{Au}(x)$ and $\Delta B^{Pd}(x)$ are negative throughout the whole concentration range, $\Delta \omega^{Au}$ and $\Delta \omega^{Pd}$ in Figs. 3 and 4, respectively, have opposite signs, in general, which is consistent with charge transfers and valence occupation changes of opposite sign, as we describe below.

(e) Analysis of $\Delta \omega^{Au}$ in the dilute Au limit employing previously measured[3] Mössbauer isomer shifts yields a charge transfer to the Au atom of the same order as that derived from the Auger measurements alone. In the dilute Au alloy, therefore, the Au atoms appear to gain around 0.2 sp electrons,[3] compensated by a loss of about the same number of d electrons. Employing the dilute Au alloy results as upper limits of the valence-electron occupation changes at intermediate compositions allows us to conclude that the charge transferred to Au is very small in this alloy system so that the d- and sp occupation changes basically compensate one another (the d change being negative and greater than in the dilute Au alloy, where it is around -0.2 electrons/atom).

(f) For noble-metal atom A, our experimental determination of $\Delta \omega^A(x)$ is exactly the definition[36,37] of the Auger parameter shift, $\Delta \xi^A$. Comparison with pure noble-metal results[22,23,36] suggests that, whenever $\Delta \xi^A$ is small for a neutral atom [the term "small" in this sense means $\Delta \xi^A \ll \xi^{Au} - \xi^{Pt} \simeq 4$ eV (Ref. 22) or $\Delta \xi^A \ll \xi^{Cu} - \xi^{Ni} \simeq 5$ eV (Ref. 36)], the excited-atom version of the QAM (Refs. 14 and 15) is valid and the ground-state valence-electron configuration is similar (i.e., the number of d holes is small) in both the alloy and pure A, since both the one- and two-core-hole states in the Auger process correspond to full local d DOS. The experimental determination of $\Delta \xi^A$ derives from its definition,[36,37] even though evaluation of $\Delta \omega^A \simeq \Delta \xi^A$ de-

pends upon the relation $\Delta \varepsilon^A \simeq -\Delta E_F^A$, so that this conclusion is independent of our assumptions. The result that $\Delta \omega^A$ is small, therefore, is seen from this point of view as intimately related to the small number of ground-state d holes in both the alloy and the pure noble metal, in agreement with extraction of valence occupation changes from XPS binding-energy shifts (at least in Au).

(g) Although determination of $\Delta \omega^{Pd}$ is straightforward, absence of such independent measurements of occupation changes as isomer shifts complicates the analysis in this case. By considering $x = 0.5$, where the Pd and Au charge transfers are equal and opposite in sign, and using the dilute Au results as upper limits on the charge transfer, it appears that the magnitude of the Pd sp-occupation change is small and negative. At lower Pd concentrations, the derived values of $\Delta \omega^{Pd}$ displayed in Fig. 4 seem to be consistent with little charge transferred to the Pd and a net loss of valence-conduction electrons (net gain of d electrons), as opposed to the case of Au. This conclusion agrees with observations[39] of Pd virtual bound states by means of XPS valence-band difference spectra in $Au_{0.95}Pd_{0.05}$.

The result that there appears to be little charge transfer in general, that it seems that Au loses whereas Pd gains d electrons and that the magnitude of the d-occupation change is small (of the order of tenths of electrons/atom) is in agreement with previous reports.[1-4,24-32] Indeed, models[7,29] in which the redistribution of valence occupations is caused by hybridization changes, rather than by charge transfer between atoms, appear quite plausible in this context.

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