Charge redistribution in Au-Ag alloys from a local perspective

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From x-ray-absorption near-edge-structure (XANES) measurements, we have obtained direct evidence for 5*d* charge depletion at the Au site for both concentrated and dilute Au-Ag alloys. This observation, together with x-ray photoemission of Au 4*f* and Ag 3*d* core levels, shows that Au gains non-*d* conduction charge and loses *d* charge while Ag gains *d* charge and loses non-*d* conduction charge; the net charge flow is negligibly small in accordance with the principle of electroneutrality. The sensitivity of XANES in probing small changes in the Au 5*d* charge redistribution ($\sim 0.02d$ count) and relativistic effects in alloying is noted.

Nobel-metal alloys of Cu, Ag, and Au have been considered prototypes for the studies of alloys with full *d* bands and the conventional Friedel charge-screening theory.[1] In the latter, the itinerant conduction electrons screen impurities, resulting in a radially oscillatory screening charge distribution, the *d* bands are full, and the *d* electrons play little role in the alloying process. Experimentally, NMR (Ref. 2) (Cu and Ag) and Mössbauer[3–5] (Au) were among the earliest techniques used in the study of local charge redistribution in these alloys. It has been realized for some time from Mössbauer isomer shifts[3–5] that the *s*-electron density at the Au nucleus always increases in Au alloys as the difference in electronegativity (Au is the most electronegative metallic element) between Au and the host increases. In order to determine whether or not the *s*-electron density trend was reflected in the x-ray photoemission spectroscopy (XPS) core-level energy shifts, Watson, Hudis, and Perlman[6] reported an observation of an apparent opposite trend of Au 4*f* binding-energy shifts relative to isomer shift and electronegativity predictions in Au-Ag and other Au alloys. They proposed a charge-compensation model with which both the Mössbauer and the XPS observations can be accounted for. In this scheme, the *d* band is active in alloying; the non-*d*-charge (*sp* conduction band, primarily *s* character) flow onto an Au site[7] is positive and is largely compensated by accompanying Au 5*d* charge depletion; the net charge flow is small (<0.1 electron), and in accord with electronegativity considerations.

Charge redistribution in Au-Ag alloys is of particular interest, since both components are completely miscible, have fcc structure and full *d* bands, and there is substantial 5*d*-4*d* overlap that is responsible for the Au *d*-band width in Au-Ag alloys that narrows little in concentrated alloys[8] but narrows substantially in diluted alloys.[9] From these properties, it is expected that charge redistribution is more subtle in this system than in the Au-metalloid intermetallics[6,10] in which the metalloid does not have overlapping *d* bands. In addition, it was also suggested,[6] albeit with less certainty, that the direction of charge flow at the Ag site in Au-Ag alloys is opposite to Au. Despite the success of this charge-compensation mechanism in explaining the results qualitatively, the potential model it employs involves several terms, each of which has large uncertainties. The objective of this work is (a) to obtain the much needed independent evidence to show quantitatively that the Au 5*d* charge depletes in Au alloys generally with a system in which charge redistribution is very small, and (b) to elucidate the sensitivity of Au *L*-edge x-ray-absorption near-edge structure (XANES), a local probe, in the detection of very small Au 5*d* count changes and corresponding angular momentum characteristics of Au 5*d* states in Au-Ag alloys.

A series of Au-Ag alloys ($Au_{0.75}Ag_{0.25}$, $Au_{0.67}Ag_{0.33}$, $Au_{0.25}Ag_{0.75}$, and $Au_{0.05}Ag_{0.95}$) has been studied. Emphasis is placed on the locally sensitive parameters: Au $L_{2,3}$-edge XANES "white lines," Au 4*f* core-level shifts, Ag 3*d* core-level shifts, and accompanying satellite structures. From the results emerges a picture that clearly shows that the *d*–non-*d* charge-compensation mechanism is indeed operating in Au-Ag alloys, a system expected to experience strong *d*-*d* interaction and relatively small local charge redistribution.

Au-Ag alloys were prepared from metals of high purity, as described elsewhere,[6] and the samples were rolled to foils with thicknesses of less than one absorption length at the Au L_3 edge. Au *L*-edge XANES measurements were recorded at the X-11A beamline of the x-ray ring (2.5 GeV) at the National Synchrotron Light Source (NSLS) using a Si(111) double-crystal monochromator. XPS experiments were made with monochromatic Al $K\alpha$ x rays in a small-spot-size Surface Science XPS spectrometer at a resolution of ~ 0.5 eV.

All the alloy Au $L_{3,2}$ spectra exhibit a white line, a sharp absorption feature just above the threshold.[11] The Au L_3 XANES of $Au_{0.75}Ag_{0.25}$, $Au_{0.05}Ag_{0.95}$, and pure Au normalized to edge jump are shown in Fig. 1. The pure-Au spectrum is used to account for the atomic edge jump as well as the unoccupied 5*d* contribution in pure Au. After subtraction of the pure-Au spectrum, the area (A_3 and A_2) under the "white line" including up to ~ 15 eV above the edge jump is obtained by integration.[12]

These areas are related to the change of the 5*d* hole population relative to pure Au. The results are shown in Table I.

The shifts of Au $4f_{7/2}$ and Ag $3d_{5/2}$ levels in the alloys relative to pure elements are listed in Table II together with the shift and intensity of the Ag 3*d* satellite (Fig. 2). No such satellite is observed in the Au 4*f* spectra, indicating that it is primarily due to intrinsic energy loss (shakeup) at the Ag site.

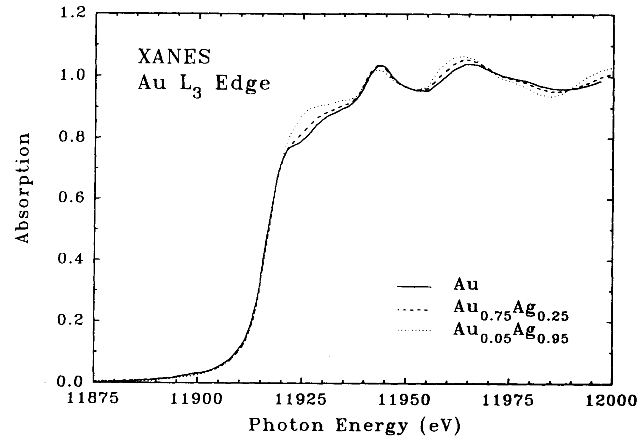

FIG. 1. Au L_3 XANES of $Au_{0.75}Ag_{0.25}$, $Au_{0.05}Ag_{0.95}$, and Au. All the spectra are aligned at E_3 and normalized to the edge jump.

Let us first focus on the Au $L_{2,3}$-edge XANES results. It is well established that the presence of a white line at the $L_{2,3}$ edge in metals is indicative of unoccupied density of *d* states ($2p \rightarrow d$ dipole transition)[13–16] in the vicinity of the Fermi level.

The most striking example of the sensitivity of a white line to the presence and absence of unoccupied 5*d* states and their angular momentum characteristics has been noted by Mott[17] in the case of Pt, which exhibits a white line at the L_3 edge but none at the L_2 edge. Mott attributed this observation to the presence of unoccupied $d_{5/2}$ states at the Pt site, which can be probed with the $2p_{3/2} \rightarrow 5d_{5/2}$ dipole transition.[17] While both Au L_3 and L_2 edges exhibit no white lines, a close examination of the Au data, however, shows that although no intense spikes are observed at these edges, conventionally regarded as "no white lines," absorption intensities arising from bound-to-localized-state transitions are unmistakably present at the threshold. For example, Lytle[16] has shown that there exists a small white line at the Au L_3 edge in accord with the band calculations of Mattheiss and Dietz (MD) (Ref. 14) and Nemoshkalenno *et al.*,[18] who show that there are unoccupied density states of $d_{5/2}$ and $d_{3/2}$ character in the vicinity of the Fermi level due to *s*-*p*-*d* hybridization. More importantly, MD have shown[14] that the difference in the white-line intensity between the Pt L_3 and L_2 edges is indeed related, at least semiquantitatively, to the populations of the $d_{5/2}$ and $d_{3/2}$ holes (henceforth denoted $h_{5/2}$ and $h_{3/2}$, respectively) by the following expressions:

$$A_3 = C_0 E_3 (R_d^{2p})^2 \left[\frac{6h_{5/2} + h_{3/2}}{15} \right] , \tag{1}$$

$$A_2 = C_0 E_2 (R_d^{2p})^2 \left[\frac{h_{3/2}}{3} \right] , \tag{2}$$

where A_3 and A_2 are the areas under the white line, C_0 is a constant characteristic of the element, and E_3 and E_2 are the threshold energies of L_3 and L_2 edges, respectively. R_d^{2p} is the radial transition matrix element.[14]

We show below, with a comparison of the difference between A_3 and A_2 in both Pt and Au $L_{3/2}$ edges of the pure element, that these equations can be used to obtain semiquantitative *d*-hole counts for the Au alloys. In the same spirit of the calculations of Brown, Peierls, and Stern,[13] MD,[14] and Mansour, Cook, and Sayers,[15] we compare the experimental and theoretical differences in white-line areas for Pt and Au in pure elements using the following expressions:

$$A_{\text{expt}} = A_{3(\text{expt})} - a A_{2(\text{expt})} , \tag{3}$$

$$A_{\text{theor}} = A_{3(\text{theor})} - a A_{2(\text{theor})} , \tag{4}$$

where A_{expt} and A_{theor} are the experimental and theoretical differences between the L_3 and L_2 edges when they are aligned; *a* is an experimentally determined factor used in the normalization, and is 2.25 for Pt and 2.20 for Au. Figure 3 shows a comparison of the Au L_3 and L_3 XANES and the difference in white-line areas from

TABLE I. Au $L_{2,3}$-edge XANES white-line area and derived parameters.

Sample	White-line area[a] (eV cm^{-1}) A_3	A_2	Au 5*d* hole distribution[b] $\Delta h_{5/2}$	$h_{5/2}$	$\Delta h_{3/2}$	$h_{3/2}$	$\Delta h_{5/2}/\Delta h_{3/2}$	$h_{5/2}/h_{3/2}$	Δh_t	h_t
$Au_{0.75}Ag_{0.25}$	645	172	0.018	0.301	0.0068	0.125	2.8	2.41	0.025	0.426
$Au_{0.67}Ag_{0.33}$	605	212	0.017	0.300	0.0084	0.126	1.9	2.38	0.023	0.426
$Au_{0.25}Ag_{0.75}$	1322	684	0.035	0.318	0.027	0.145	1.3	2.19	0.064	0.463
$Au_{0.05}Ag_{0.95}$	1695	878	0.045	0.328	0.035	0.153	1.3	2.14	0.085	0.481

[a] Integrated area up to 15 eV above the threshold after background subtraction, the Au edge jump coefficients from McMaster *et al.* (NIT Service, Springfield, Va., 1969) were used in the calculation; see text.

[b] Calculated according to published procedure (see Ref. 15); all Δh_j values are changes relative to pure Au. All h_j values are $\Delta h_j + h_j$ of pure Au; uncertainty arises from the average of the results from more than one spectrum and is ~10%.

TABLE II. Relevant experimental and derived parameters (relative to pure elements).

Sample	ΔE (Au $4f_{7/2}$)	Δn_c[a]	Δn_d[a]	δ[b]	ΔE (Ag $3d_{5/2}$)	ΔE(sat.)	I(sat.)[c]
$Au_{0.75}Ag_{0.25}$	0.04	0.046	−0.049	0.001	−0.25	2.5	≪1%
$Au_{0.67}Ag_{0.33}$	0.03	0.068	−0.073	−0.003	−0.24	2.73	1.1%
$Au_{0.25}Ag_{0.75}$	0.13	0.139	−0.141	−0.001	−0.11	3.37	1.3%
$Au_{0.05}Ag_{0.95}$	0.13	0.177	−0.179	0.001	0.0	3.71	3.5%
Ag					0.0	3.79	4.5%

[a] Derived from Mössbauer data of Ref. 5, ±0.002; see Ref. 10 for details.

[b] Calculated according to Eqs. (1) and (2); uncertainty is ±0.02.

[c] Relative to the intensity of the main peak, error ±0.1%.

which $A_{\text{expt}}=0.65\times10^4$ cm^{-1} eV is obtained. Using the d-hole population and the R value of MD for Pt,[14] we obtain $A_{\text{theor}}=0.40\times10^4$ cm^{-1} eV for Au, in reasonable accord with the experiment. This set of values also compares favorably with those of Pt ($A_{\text{expt}}=1.86\times10^4$ cm^{-1} eV, $A_{\text{theor}}=1.57\times10^4$ cm^{-1} eV) (Ref. 14) and the corresponding d holes of the calculation of MD (Au: $h_{5/2}=0.283$, $h_{3/2}=0.118$; Pt: $h_{5/2}=1.000$, $h_{3/2}=0.344$). The discrepancy between theory and experiment most likely arises from the use of the R value as well as the hole counts. This, however, does not have a significant effect on the semiquantitative analysis presented here.

Returning to the alloys, it is immediately apparent from Fig. 1 and Table I that A_3 and A_2 (hence the Au 5d hole) increase upon dilution. This observation thus provides direct evidence for the first time for d charge depletion at the Au site in Au-Ag alloys. Quantitatively the change of the Au 5d holes $\Delta h_{5/2}$ and $\Delta h_{3/2}$ relative to pure Au can be related to the white-line areas to the first approximation[15] by

$$\Delta h_{5/2}=(2.25A_3-0.5A_2)/C\ , \tag{5}$$

and

$$\Delta h_{3/2}=3A_2/C\ , \tag{6}$$

where C is a constant characteristic of Au.[19] The results are shown in Table I together with the total d holes h_t based on MD's calculations of pure Au.[14] It is interesting to note that the change of d-hole population is only a small fraction of that of the pure Au and that the $\Delta h_{5/3}/\Delta h_{3/2}$ hole ratio (Table I) exhibits a factor of 2 decrease upon dilution, while the ratio of the total d hole $h_{5/2}/h_{3/2}$ decreases steadily from the concentrate to the dilute alloy, indicating that relativistic effects are very sensitive to Au-Au interaction. This trend is quite different from those of Au-Cu and Au nontransition alloys.[10,20] The details of such a comparison will be discussed elsewhere. The total change in Au 5d hole population Δh_t (relative to pure Au) derived from the XANES data varies from 0.025 to 0.08, very small in comparison to the total d holes of 0.401 in pure Au (Ref. 14) (Table I).

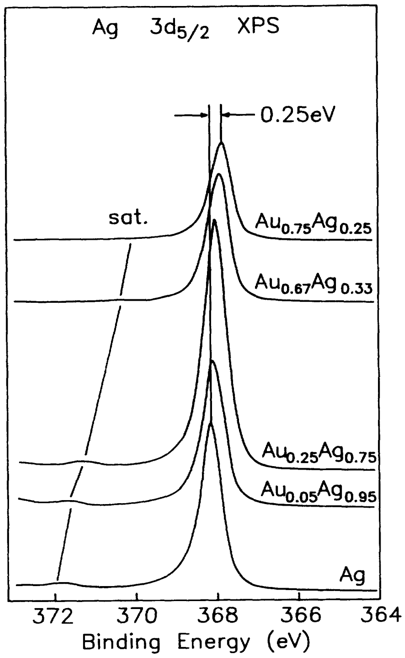

FIG. 2. Ag 3d core-level spectra of Au-Ag alloys.

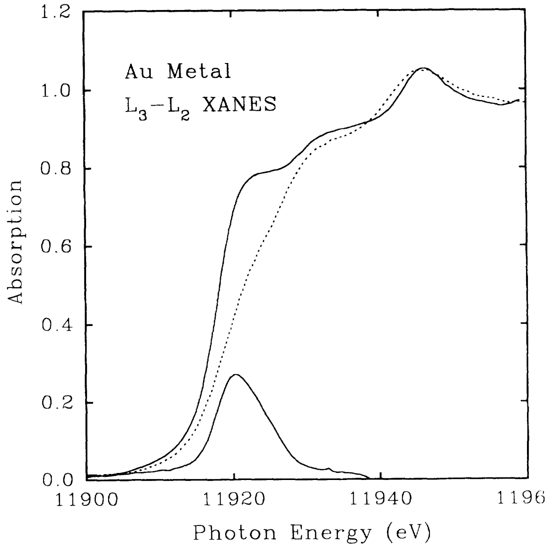

FIG. 3. Normalized Au L_3- and L_2-edge XANES aligned at the L_3 edge; the Au L_2 XANES have been multiplied by 2.2. The difference spectrum A_{expt} is also shown.

We next compare the Δh_t values derived from Au $L_{3,2}$-edge white lines with the d charge transfer Δn_d derived from the Au $4f_{7/2}$ shifts and the Mössbauer isomer shifts[21] (Table II). Using the model of Watson *et al.* with appropriate Coulomb integrals,[9,21] the $5d$ count depletion at the Au site Δn_d and the net charge flow δ onto the Au site for all the alloys can be obtained according to the expressions[6,9]

$$\Delta E_{\mathrm{Au}} = -\Delta\phi - \Delta n_c[F^0(4f,c) - F^0(4f,5d)] - \delta[F^0(4f,5d) - F_{\mathrm{latt}}] + \left[\frac{dE}{dV}\right]\Delta V , \qquad (7)$$

and

$$\delta = \Delta n_c + \Delta n_d , \qquad (8)$$

where $\Delta\phi$ is the work-function change, F^0 terms are the screened Coulomb integrals, F_{latt} is a Madelung-like term evaluated by placing a charge at the Wigner-Seitz radius,[6] and the last term is for volume correction and is neglected in this analysis. The results (Table II) show that within the uncertainty of the parameters,[22] there is negligible net charge flow ($\delta = +0.001$ to -0.005), and that the d-hole count derived from XANES is smaller than Δn_d, as observed previously.[10] This discrepancy is most likely due to an overestimated Δn_d and/or the neglect of p contributions. These results can actually be used to refine the charge-compensation model.[6]

We now consider the Ag site. Upon dilution, the alloy $3d$ level generally shifts to lower binding energy. Since the position of the Fermi level in Ag and Au is nearly the same, and the Coulomb interaction $F^0(3d-4d)$ is significantly larger[6] than $F^0(3d-5s)$ in Ag, this shift indicates, within the single-particle approximation, that Ag gains d charge. The energy shift [ΔE(sat.), Table II] of the Ag $3d$ satellite decreases as Ag becomes more dilute in Au. This shift is accompanied by a significant decrease in intensity. The satellite, which is not observed in the Au $4f$ spectrum, is attributed to a shakeup involving excitation of Ag d-band electrons into unoccupied states of nl (mostly d) character.[23] Thus, it depends on both the occupied and unoccupied states. Hillebrecht *et al.*[23] observed similar core-level satellite behavior in a series of Ni and Pd alloys and attributed their observation to d-band filling; that is, the smaller the d-hole population above the Fermi level, the weaker the satellite intensity. We propose that a similar mechanism is operating for the Au-Ag alloys. There are, however, some differences between the two systems. First, in Ni and Pd, the d band is not fully occupied and lies across the Fermi level, and there exist localized unoccupied d states at the Fermi level. In Ag, however, the d band is nominally full and corelike (~ 5.5 eV below the Fermi level), although there is unoccupied d character above the Fermi level due to s-d rehybridization. Second, in the Ni and Pd alloys,[23] the d band usually moves away from the Fermi level, while in Au-Ag alloys the Ag d character may spread towards the Fermi level as the result of Au-Ag d-d interaction.[9] These differences are consistent with the observed trend of the satellite position and intensity in both systems. Since all the evidence indicates a neutral Au at the Au site (hence a neutral Ag at its site), and Ag gains d charge from both core-level and satellite observations, we are led to the conclusion that Ag redistributes its non-d valence charge to the previously unoccupied d channel to maintain electroneutrality locally in Au-Ag alloys. Our recent Ag $L_{2,3}$-edge x-ray-absorption measurement of these Ag-Au alloys confirms that Ag indeed gains d character upon dilution in Au.[24]

Finally, it should be noted that the involvement of p charge redistribution has not been explicitly addressed by the charge-compensation model, nor has it been dealt with in the core-level binding-energy analysis. Despite this simplification, the Au $L_{2,3}$-edge XANES results, which are independent of the potential model used in the combined XPS core-level and Mössbauer analysis required by the charge-compensation mechanism,[6] show the same d-charge depletion trend upon alloying. This agreement lends some credibility to the charge-compensation model. More experimentation is needed to address the p-charge question, including the nonchemical tailing charge of p characters recently addressed by Watson, Davenport, and Weinert.[25] It is also interesting to note that the direction of d-charge transfer reported here differs from those observed by Thomas and Weightman[26] and Wertheim *et al.*[27] in the study of Au-Mg, Au-Zn, and Au-Cs alloys where a gain of d charge at the Au site was concluded. It is still not clear why there is such a discrepancy. It may be due to the different nature of the hosts (Au-Ag has overlapping d bands while the other hosts and Au have no overlapping d bands) or the analytical model. It now becomes very desirable to carry out XAFS measurements of AuMg, AuZn, and AuCs to further investigate this discrepancy.

We have reported observations on the electronic structure of Au-Ag alloys from a local perspective using x-ray-absorption and XPS core-level measurements. All the results clearly show that Au loses d charge while Ag gains d charge. What remains to be addressed is the role of p character and tailing charges from neighboring sites in Au-Ag alloying.[25]

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[11] Historically, strong absorption at the threshold appeared on the photographic plate as a white line. In this context, white line refers to extra absorption intensity within ~10 eV above the threshold relative to the intensity of the pure Au.

[12] Although this choice is somewhat arbitrary, it accounts for all the sharp white lines observed in other Au bimetallic compounds where unoccupied d states are localized at the Fermi level, and core lifetime (~8 eV).

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