

## Electronegativity and electron binding in gold alloys\*

T. S. Chou, M. L. Perlman, and R. E. Watson

*Departments of Chemistry and Physics, Brookhaven National Laboratory, Upton, New York 11973*

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Measurements were made of the Au core-electron binding-energy shifts which occur when Au metal is made the minor constituent in alloys of Pd, Pt, and Ni. These results and binding-energy shifts previously reported for alloys with Ag, Al, and Sn were combined with Mössbauer isomer-shift and work-function data to derive estimates for the net charging of the Au sites in these systems. Au turns out to be negative in all cases to the extent of  $\sim 0.1e$ , except for Au-Pt where the charging is less. Although considerably greater Au  $s$  density increases are demonstrated by the Mössbauer data, they are largely compensated by depletion of the  $d$  count. The trend in host-to-Au charge behavior is qualitatively in accord with the Pauling electronegativity scale.

### INTRODUCTION

In an important paper, Barrett *et al.*<sup>1</sup> reported studies of gold as an impurity in a variety of metal hosts; they measured Mössbauer isomer shifts, which provide a measure of  $s$ -like charge density at the Au nucleus, and concluded that the  $s$ -like density in all the alloys is increased relative to that in pure Au. This conclusion is consistent with the electronegativity scale of Pauling, which assigns to Au the greatest electronegativity amongst the metallic elements, but it is inconsistent with other such scales based on considerations of alloy solubility and alloy heats of formation. Now the alloying properties of Au involve not only the conduction bands, primarily of hybridized  $s$ - $p$  character, but also the  $d$  bands, which lie several eV below the Fermi level. In a study of Au impurity in Ag, Sn, and Al hosts,<sup>2</sup> the core level shifts deduced from x-ray photoelectron spectroscopy were employed together with isomer shifts to deduce the *net* charge flow. The picture which emerged was one in which there is appreciable depletion of  $5d$  count at Au sites, owing to hybridization (i.e., covalent mixing) of the occupied  $d$  levels, accompanied by a relatively small net increase in charge. This is not altogether surprising since Ag, Sn, and Al are significantly less electronegative than Au on any scale. The present communication is a report of the extension of the study to alloys of Ni, Pd, and Pt, elements which are sometimes<sup>3,4</sup> thought to be more electronegative than Au. It turns out that in these cases as well, net charge flow appears to be onto Au sites.

Alloys of Ni, Pd, and Pt with Au are convenient to treat; the constituents are face-centered cubic and there is solubility over the full concentration range. What is more, the lattice volume of any of these alloys is, to a good approximation, the average of the atomic volumes of the pure constituents; i.e., for an alloy with Au concentration  $C_{Au}$

$$V_{\text{alloy}} = (1 - C_{Au})V_{\text{host}} + C_{Au}V_{Au}, \quad (1)$$

and thus the volumes characteristic of the pure metals,  $V_{\text{host}}$  and  $V_{Au}$ , can be assigned to the constituent atoms of the alloy. This obviates volume corrections to either the chemical or isomer shifts.

### EXPERIMENTAL PROCEDURES AND RESULTS

All alloys were prepared from pure metals by arc melting in argon inert atmosphere in a water-cooled copper crucible. To ensure homogeneity, the resulting ingots were turned over and remelted several times. The compositions reported in Table I are the atom ratios taken for the alloy preparation. The ingots were filed into roughly cylindrical shapes for introduction into the photoelectron spectrometer, a Varian IEE-15 instrument with a Mg  $K\alpha_{1,2}$  x-ray source. Alloy surfaces were cleaned by glow-discharge ion sputtering in purified Ar at about 20 mTorr in a chamber attached to the spectrometer. Depending on the surface condition, a negative potential of from 1 to 2 kV was applied to it for 1–5 min. Photoelectron spectra from the  $4f$  levels of Au were measured with the instrument set to transmit 50-eV electrons.

After each alloy run the spectrum of a pure-gold standard was taken to check the stability of the instrument. Spectra were analyzed by computer fitting Gaussian line shapes and smooth backgrounds to the data. Uncertainties in the binding energies reported in Table I are about 0.05 eV.

### ANALYSIS OF RESULTS

The chemical shift, upon alloying of a core-level binding energy of Au, may be represented as a sum of several contributions:

$$\Delta E_B = -\Delta n_d F_d - \Delta n_c F_c + \delta \mathcal{F}_{\text{latt}} - \Delta \Phi(\text{Au} \rightarrow \text{alloy}). \quad (2)$$

TABLE I. Au-site charging ( $\delta$ ) in Au alloys as derived from Eq. (4) and the several quantities: measured Au 4*f*-level binding-energy shifts ( $\Delta E_B$ ); changes in conduction-electron count ( $\Delta n_c$ ) evaluated from Mössbauer isomer shifts; work-function differences ( $\Delta\Phi$ ); and the calculated Coulomb-interaction terms  $F_d$ ,  $F_s$ , and  $\mathfrak{F}_{\text{latt}}$ .

Alloy	$\Delta E_B = E_B(\text{Au in alloy}) - E_B(\text{Au } 100\%)$ (eV)	$\Delta n_c (F_s - F_d)$ (eV)	$\Delta\Phi = \Phi_{\text{host}} - \Phi_{\text{Au}}$ (eV)	$\delta(\mathfrak{F}_{\text{latt}} - F_d)$ (eV)	$\delta$	$\Delta n_c = n_c(\text{Au in alloy}) - n_c(\text{Au } 100\%)$
Au <sub>0.053</sub> Ag <sub>0.947</sub>	+0.30 ± 0.05	-0.3	-0.8 ± 0.5	-0.8	0.1	0.1
AuAl <sub>2</sub>	+1.35 ± 0.05	-1.9	-0.7 ± 0.4	-1.2 <sub>5</sub>	0.1 <sub>4</sub>	0.6
AuSn <sub>4</sub>	+1.10 ± 0.05	-0.9	-0.8 ± 0.2	-0.6	0.07	0.3
Au <sub>0.106</sub> Pd <sub>0.894</sub>	-0.40 ± 0.05	-0.6 <sub>5</sub>	+0.2 ± 0.2	-0.8 <sub>5</sub>	0.1 <sub>0</sub>	0.2
Au <sub>0.101</sub> Pt <sub>0.899</sub>	-0.30 ± 0.05	-0.3	+0.3 <sub>5</sub> ± 0.2	-0.2 <sub>5</sub>	0.03	0.1
Au <sub>0.101</sub> Ni <sub>0.899</sub>	+0.10 ± 0.05	-1.2	-0.0 <sub>5</sub> ± 0.2	-1.1 <sub>5</sub>	0.1 <sub>3</sub>	0.4

Here  $F_d$  and  $F_c$  are the changes in core one-electron energy resulting from the addition at the Au site of a single  $d$  or conduction electron, respectively. It is noted that valence-electron relaxation at the Au site, which necessarily accompanies any change in  $d$  or conduction-electron charge, itself affects the core electron potential and should be taken into account in any estimate of the  $F$ 's.<sup>5</sup> As the third term indicates, any net charge flow,

$$\delta = \Delta n_d + \Delta n_c, \quad (3)$$

gives rise to a Madelung-like contribution  $\delta\mathfrak{F}_{\text{latt}}$  to the core level shift, owing to the presence of this charge in the surrounding host atoms.

Now the binding energies are actually measured relative to the individual Fermi levels of the samples. These values may be referred to a *common* zero, the vacuum zero external to the samples, by adding the work function  $\Phi$ . In Eq. (2), then, the reference to this common zero is taken into account with the final term  $\Delta\Phi$ . Equations (2) and (3) may be combined to eliminate one unknown,

$$\Delta E_B + \Delta n_c(F_s - F_d) + \Delta\Phi(\text{Au} \rightarrow \text{alloy}) = \delta(\mathfrak{F}_{\text{latt}} - F_d). \quad (4)$$

To arrive at Eq. (4)  $F_c$  has been evaluated, as an approximation, in terms of an atomic 6*s* function normalized to the Wigner-Seitz volume; subsequently this quantity is designated  $F_s$ . The object of this exercise is, of course, to estimate  $\delta$  by use of Eq. (4), in which  $\Delta E_B$  is determined as outlined above, values for  $\Delta n_c$  are based on Mössbauer isomer shift data,  $\Phi$  values are from the literature, and the  $F$ 's are calculated. Several factors are omitted from Eqs. (2) and (4). As already discussed, volume effects are unimportant and are neglected.<sup>6</sup> Perhaps more important is the neglect of change in screening of the final-state 4*f* hole. However, since all the samples

are good metals and should be approximately equal in screening ability, it is reasonable to expect that quantitative but not qualitative error should be associated with neglect of screening differences.

What is probably most important, finally, is that  $F_c$ ,  $F_d$ , and  $\mathfrak{F}_{\text{latt}}$  in Eq. (4) are calculated with reference to the crystal zero rather than the vacuum zero. These two references differ by the dipole barrier  $D$  present at the metal surface.<sup>7</sup> Theory must be relied upon for dipole-barrier estimates. Unfortunately, there exist no such results which are applicable to transition metals, and quantitative results for metals such as Au, Ag, Sn, and Al are poor. Modification of Eq. (4) by inclusion of  $\Delta D$  estimates for these metals leads to increases in the  $\delta$  values of roughly a factor of 2.

In addition to the experimental  $\Delta E_B$  values obtained here, there are included in Table I those reported previously for the Ag-, Sn-, and Al-based alloys. Work functions from the tabulations of Riviere,<sup>8</sup> Eastman,<sup>9</sup> and Haas and Thomas<sup>10</sup> were used to obtain the  $\Delta\Phi$  values. The factors  $F_s - F_d$  and  $\mathfrak{F}_{\text{latt}} - F_d$  are calculated to be  $-3.1 \pm 0.3$  and  $-9 \pm 2$  eV, respectively. As mentioned,  $\Delta n_c$  was obtained from measured Au isomer shifts<sup>1</sup>  $S$  with the calibration

$$\Delta n_c = -0.086S,$$

where  $S$  is in mm/sec. This calibration involves, along with several better known quantities, estimates of the fraction of  $s$  character in the conduction-band states, estimates here based on experience with Knight-shift hyperfine constants.<sup>11</sup> An uncertainty of about 25% in the calibration constant has no great effect on the conclusions. From the quantities in the last column of the table and the value above for  $\mathfrak{F}_{\text{latt}} - F_d$  we find that  $\delta \sim +0.1e$ , except in the case of AuPt, where it is about one-fourth as large. It is tempting to examine the  $\Delta n_c$

and  $\delta$  quantities in detail, in particular to see whether the chemistry of Au, that is the interplay of  $\Delta n_d$  and  $\Delta n_c$ , differs between transition- and nontransition-metal hosts. Unfortunately, the uncertainties are such that one cannot go beyond observing that  $\Delta n_c$  and  $\Delta n_d$  are opposite in sign and that  $\Delta n_c$  dominates to determine the sign of  $\delta$ .

### CONCLUSIONS

In Fig. 1 the resulting  $\delta$  values are plotted versus the Pauling electronegativities of the host metals.<sup>12</sup> There is a distinct suggestion of a monotonic trend, consistent with charge flow always onto the Au site; given the uncertainties in the  $\delta$ 's, it appears that the Pauling scale and the charge flow correlate fairly well. Incidentally, the plot of  $\Delta n_c$  versus this scale, also shown in Fig. 1, does<sup>1</sup> about as well. As noted at the outset, there are other scales on which Au is not the most electronegative of the metals; the success of some of these in correlating certain alloy properties is an indication of the complexity of the physics and chemistry of alloying processes. It would appear that "electronegativity" as used in these scales does not rest solely on the tendency for the displacement of charge.

Finally, we should note that the net charge flow is small compared with the formal charges often

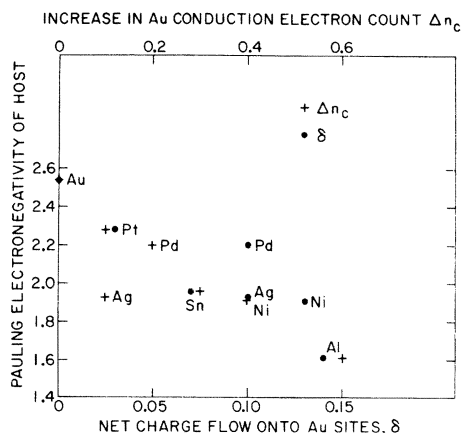


FIG. 1. Relationship between Pauling electronegativity of host metal and net charge flow onto Au sites in dilute binary alloys of Au. Change in conduction-electron count also is shown.

assigned atoms in solids. We believe that site charges of  $\sim 0.1e$  are characteristic of what can be maintained in metallic systems.

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<sup>6</sup>There is a modest deviation from Eq. (2) in the case of  $\text{AuAl}_2$ , for which we estimate a contribution to  $\Delta E_B$  due to volume effects of  $< 0.3$  eV. This is not important to the present results.

<sup>7</sup>F. Seitz, *The Modern Theory of Solids* (McGraw-Hill, New York, 1940), p. 396.

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<sup>12</sup>Electronegativities are from the calculations by A. L. Allred [*J. Inorg. Nucl. Chem.* **17**, 215 (1961)] which are based on thermochemical data. These data and values given by L. Pauling [*Nature of the Chemical Bond*, 3rd ed. (Cornell U. P., Ithaca, N.Y., 1960), p. 93] for the host elements of concern differ by an average of 0.08 units.