

Electronic behavior in alloys: Gold-non-transition-metal intermetallics

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Chemical effects (charge-transfer and valence-band behavior) upon alloying in Au alloys have been studied in a series of Au-Cd, Au-In, Au-Sn, Au-Sb, and Au-Te intermetallics by ^{197}Au Mössbauer and x-ray photoemission measurements. For these alloys, the Mössbauer isomer shifts (2.0–4.7 mm sec $^{-1}$ relative to Au) indicate significant increases of valence s character at the Au sites, whereas the Au-4*f* binding-energy shifts (0.2–1.35 eV relative to Au) indicate apparent charge depletion. This study, together with previous observations, confirms that there is little net charge flow between Au and host-metal atoms upon alloying, i.e., that the increase of predominantly s -like conduction-electron count, Δn_c , at a Au site is largely compensated by a depletion in 5*d* count, Δn_d . It is found from an analysis that the net charge flow at the Au site, $\delta = \Delta n_c + \Delta n_d$, is approximately 0.1 electron and that the ratio $\Delta n_c/\Delta n_d$ is surprisingly constant given the various numerical uncertainties of the analysis. It thus appears that the d bands are actively involved, through hybridization, in alloying, and that such s - d compensation is a general characteristic of Au alloys. Substantial hybridization of the Au d bands with the Au non- d states and with the valence states of main-group metal atoms is observed in the valence-band spectra. The relationship of this hybridization to the d and non- d charge-transfer effects inferred from the core level and Mössbauer shifts is discussed. It is also found that in some cases the isomer shifts of the dilute alloys are similar to those of the intermetallic compounds, indicating that the local order around the Au site in these dilute alloys is similar to that in the intermetallic compounds.

I. INTRODUCTION

In several recent investigations¹⁻³ of charge flow in Au alloys using Mössbauer and x-ray photoemission techniques, it has been found that the traditional picture of charge screening of impurity atoms in alloys is not necessarily adequate for the description of charge flow in Au alloys. In the Friedel charge-screening theory,⁴ the approximately free conduction electrons screen impurities. What has emerged from these recent results¹⁻³ is a picture in which there is a significant increase in valence s character at the Au site, an increase compensated by an almost equivalent loss of d character. To further pursue the question of whether such s - d compensation is a general characteristic of Au alloys, we have studied a series of Au alloys with Cd, In, Sn, Sb, and Te as the hosts. These systems are chosen for three reasons. First, Au forms at least one intermetallic compound with the main group host metals and the molecular volumes of these compounds are almost equal to the sum of the atomic volumes⁵ characteristic of metallic Au and host metals, obviating the necessity for a volume correction to the level shift. Second, Mössbauer experiments can be easily performed with Au-containing absorbers. Finally, we can observe the effects of alloying on the Au 5*d* bands in the valence-band spectra for alloys in which Au is only a minor constituent because the x-ray photoabsorption cross section of the Au 5*d*

electrons is much greater than those of the s and p electrons in the hosts, which have relatively little or no structure in their conduction bands.

In this paper, we report a systematic study of the electronic behavior of these Au-main-group intermetallics based on Mössbauer and photoemission techniques. The experimental procedures and results are given in Sec. II. The molecular volumes of the alloys are briefly described in Sec. III and the Mössbauer isomer shifts are discussed in Sec. IV. The Au-4*f* binding-energy shifts ΔE_B are analyzed, and the net charge flows δ onto Au sites are estimated in Sec. V from a model described previously.³ Valence-band spectra are discussed in Sec. VI and the conclusions are given in Sec. VII.

II. EXPERIMENTAL METHODS AND RESULTS

All the alloys were prepared from pure metals by melting appropriate amounts of Au and main-group metals in quartz capsules under H_2 or under vacuum.

Mössbauer spectra were recorded with both source and absorber at liquid-helium temperature. The spectrometer has been described by Kistner.⁶ Sources of ^{197}Au 77-keV γ rays were prepared by neutron activation of ~20-mg, 0.025-mm-thick Pt metal foils (enriched to ~97-at. % ^{196}Pt) for an hour in the high flux beam reactor at Brookhaven National Laboratory. The absorbers were prepared

as foils, or as pressed disks of powder mixed with Lucite. Spectra were calibrated with an iron foil absorber and were fitted to Lorentzian line shapes by use of a nonlinear regression program. All the spectra except those for the Au-Te series have single narrow Lorentzian line shapes. Full widths at half height are $\sim 2 \text{ mm sec}^{-1}$.

Photoelectron spectra of the Au $4f$ levels, of main-group $3d$ levels, and of the valence bands of these alloys were obtained with a Varian IEE-15 spectrometer or with a Vacuum Generators ADES 400 spectrometer which features ultrahigh vacuum under normal operating conditions (5×10^{-10} to 5×10^{-11} Torr). Alloy surfaces were cleaned in the Varian by glow-discharge ion sputtering in purified Ar at about 20 mTorr in a chamber attached to the spectrometer and by a focusing argon-ion gun at about 2×10^{-6} Torr in the VG instrument. The spectrometers were calibrated by a pure gold standard after each run. Spectra were fitted to a Gaussian-Lorentzian function.⁷ The Mössbauer isomer shifts S (relative to Au) and the Au- $4f$ binding-energy shifts (obtained at room temperature) ΔE_B are given in Table I.

III. VOLUME CONSIDERATIONS

Structural information on Au-main-group-metal alloys is well documented.^{6,8} The atomic volume

TABLE I. Mössbauer isomer shifts and binding-energy shifts of Au alloys.^a

Alloy	S (mm/sec)	$\Delta E_{Au\ 4f}$ (eV)
AuTe ₂	2.16(4)	0.30(8)
Au _{0.052} Te _{0.948}	2.24(4)	0.24(3)
Au _{0.011} Te _{0.989}	2.10(10)	
AuSb ₂	3.41(1)	0.22(2)
Au _{0.098} Sb _{0.902}	3.50(5)	
AuSn ₂	3.97(5)	1.32(5)
Au _{0.099} Sn _{0.901}	3.77(2)	1.35(5)
AuIn	3.56(1)	0.38(2)
AuIn ₂	4.64(1)	0.71(2)
Au _{0.099} In _{0.901}	4.67(2)	
Au _{0.050} In _{0.950}	4.68(2)	0.86(5)
AuCd	2.00(2)	0.30(3)
AuCd ₃	3.27(2)	0.70(5)
Au _{0.050} Cd _{0.950}	3.26(2)	0.60(5)
Au _{0.010} Cd _{0.990}	3.04(10)	
AuGa ₂	5.56(1)	1.30(5) ^b
AuAl ₂	7.07(3)	1.35(5) ^b 1.95(5) ^c
Au _{0.050} Cu _{0.950}	4.18(2)	0.50(5)
Au _{0.050} Zn _{0.950}	3.37(2)	1.09(5)
Au-Te	1.9(3) ^d	
Au-Al	7.6(4) ^d	
Au-Sn	4.3(4) ^d	

^a S and ΔE_B are relative to pure Au.

^bReference 1.

^cReference 25.

^dReference 13.

in Au is 17.0 \AA^3 whereas the atomic volumes of Cd, In, β -Sn, Sb, and Te are 21.25, 25.96, 26.96, 30.05, and 33.76 \AA^3 , respectively.⁹ For all the Au-main-group intermetallic compounds of known structure, the molecular volume derived from the lattice structure is, to a good approximation, the average of the atomic volumes of the pure constituents (Table II); i.e., for an alloy with Au atomic fraction $[C]_{Au}$,

$$V_{\text{alloy}} = [C]_{Au} V_{Au} + (1 - [C]_{Au}) V_{\text{host}}, \quad (1)$$

and thus the volumes characteristic of the pure metal can be assigned to the constituent atoms of the alloys. It is apparent from Table II that the above equation holds and that any significant changes in isomer shift and binding energy can be attributed primarily to chemical effects rather than to changes in volume characteristic of the atomic sites.^{10,11}

IV. ¹⁹⁷Au MÖSSBAUER ISOMER SHIFTS

The isomer shift of an absorber can be related to the difference of electron contact density between the source and the absorber by^{11,12}

$$S = (0.00608 Z \Delta \langle r^2 \rangle / E_\gamma) \Delta \rho(0), \quad (2)$$

where Z , the nuclear charge, and E_γ , the γ -ray energy (keV), are characteristic of the Mössbauer nucleus as is $\Delta \langle r^2 \rangle$, the change in the square of the nuclear-charge radius between the excited and ground nuclear states. $\Delta \langle r^2 \rangle$ is in 10^{-3} Fm^2 and S in mm sec^{-1} . For ¹⁹⁷Au, $\Delta r/r$ is positive.¹² $\Delta \rho(\sigma_0^3)$ is the source-absorber electron-contact-density difference, arising primarily from the difference of valence- s -electron density.

There are actually two factors which can be responsible for an increase of contact density $\Delta \rho(0)$ measured by the ¹⁹⁷Au isomer shift. An increase in the conduction-electron count Δn_c at the atomic site of Au increases $\rho(0)$, and a decrease in d count Δn_d , by decreasing the screening effect to the outer valence electrons, also increases the $\rho(0)$. Thus

TABLE II. Volume effects in Au-main-group-metal intermetallics.^a

Alloy	V_{mol} (\AA^3)	$\sum V_{\text{atom}}$ (\AA^3)
AuTe ₂	80.5	84.4
AuSb ₂	73.82	77.0
AuSn ₂	69.50	70.96
AuSn ₄	121.25	124.96
AuIn ₂	69.20	68.80
AuIn	40.23	42.82
AuCd	36.70	38.30

^a V_{atom} values are from Ref. 9 and V_{mol} values are from Refs. 6 and 8.

$$\Delta\rho(0) \propto \Delta n_c + R\Delta n_d, \quad R \sim -0.5 \text{ to } -1 \quad (3)$$

where R is the ratio of the d screening term to the non- d term.

It is expected that both terms contribute because approximate charge neutrality should be maintained in the metallic alloys, i. e., $\Delta n_c + \Delta n_d \sim 0$. A positive S value, as shown in Table I, therefore indicates that, relative to pure gold, there is an increase in s character at the Au site in all these alloys and that Δn_c is positive. This observation is consistent with very dilute Au-alloy results reported earlier by Barrett *et al.*¹³ and with Pauling's electronegativity scale,^{11,14} in which Au is assigned to be the most electronegative among the metallic elements.

A quantitative relationship between S and Δn_c has been derived previously^{2,3} as

$$\Delta n_c = -0.086S \text{ (mm sec}^{-1}\text{)}. \quad (4)$$

This calibration involves estimates of the fraction of s character in the conduction-band states based on experience with Knight-shift hyperfine constants.³ This calibration is used to derive Δn_c in the evaluation of the net charge transfer δ given in Sec. V.

Several other interesting features such as the qualitative correlation of S with periodicity of the hosts are apparent from Table I, but they are not discussed here in detail. What is probably most interesting and important is that the increase of S from one intermetallic compound to a more dilute one, such as from AuCd to AuCd₃ or AuIn to AuIn₂, saturates at dilute solution. For example, S for alloys Au_{0.052}Te_{0.948}, Au_{0.05}In_{0.95}, and Au_{0.05}Cd_{0.95} is similar to that of AuTe₂, AuIn₂, and AuCd₃, respectively. These results have the following implication: either (a) Au does not form a solid solution with the host at these concentrations even though these samples were prepared by quenching the melt from high temperatures, but instead forms a two-phase system composed of Au- M intermetallic compound and pure host, or (b) Au forms a dilute alloy in which the Au site has a nearest-neighbor shell of unlike atoms similar to that of the corresponding intermetallic compound and that this local order is associated with the S value.

In order to understand the results better without having to assume that the quenched samples are good solid solutions,¹⁵ we studied the 1-at. % -Au solid solutions in Te and Cd. The Mössbauer results again show the same trend (Table I). Furthermore, the previously reported S for very dilute Au in Te has a value equal within experimental error to those for other Au-Te alloys, i. e., S values for very dilute Au in Te,¹³ Au_{0.011}Te_{0.989},

Au_{0.052}Te_{0.948}, and AuTe₂ are 1.9 ± 0.3 , 2.1 ± 0.3 , 2.24 ± 0.04 , and 2.16 ± 0.04 mm sec⁻¹, respectively. This result strongly indicates that in each alloy system the local order at the Au site in these dilute Au-main-group-metal alloys is similar to that of the most dilute Au-main-group intermetallic compound (AuCd₃ in Au-Cd alloys, etc.). Details for the Au-Te system, which is of especial interest because of the quadrupole effects which are encountered, will be published elsewhere.¹⁶

V. CORE-LEVEL BINDING-ENERGY SHIFTS AND NET CHARGE FLOW UPON ALLOYING

It has been shown that the chemical shift upon alloying of a core-level binding energy of Au may be represented as a sum of several contributions¹⁻³:

$$\Delta E_B = -\Delta n_c F_c - \Delta n_d F_d + \delta \mathcal{F}_{1att} + \Delta \epsilon_F \text{ (Au} \rightarrow \text{alloy)}. \quad (5)$$

Here F_c and F_d are the changes in core-electron binding energy resulting from the addition at the Au site of a single conduction or d electron, respectively: valence-electron relaxation and atomic-volume renormalization² have been taken into account in the estimate of the F 's. The net charge flow

$$\delta = \Delta n_c + \Delta n_d \quad (6)$$

gives rise to a Madelung-like contribution $\delta \mathcal{F}_{1att}$, due to the presence of this charge outside the volume of the Au atom. This term, which is a Madelung sum for an ordered compound, arises, in the case of a dilute impurity, from the placement of the transferred charge δ in the immediate neighborhood of the impurity site, after the manner of Friedel theory.⁴ Equation (5) represents the relation connecting the experimental binding-energy shift ΔE_B (alloy-Au), which is measured relative to the Fermi level, with the change in electron binding energy of the core level, the ΔnF terms, calculated relative to the crystal zero and a Fermi level shift $\Delta \epsilon_F$, taken to be the difference in work function $-\Delta\phi$ (the difference in dipole barrier ΔD has been neglected in this calculation). It is necessary to include the $\Delta \epsilon_F$ term in order to bring the ΔE_B and the F terms to the same reference level. Equations (6) and (5) may be combined to arrive at

$$\Delta E_B + \Delta n_c (F_c - F_d) + \Delta\phi \text{ (Au} \rightarrow \text{alloy)} \\ = \delta (\mathcal{F}_{1att} - F_d). \quad (7)$$

Now, the net charge flow δ can be evaluated from Eq. (7), in which ΔE_B is determined experimentally, Δn_c is based on Mössbauer isomer shifts,

TABLE III. Au site charging (δ) in Au alloys.^a

Alloy	ΔE_B (eV)	$\Delta n_c(F_c - F_d)$ (eV)	$\Delta\phi$ (eV)	δ	Δn_c	Δn_d	$\frac{\Delta n_c}{\Delta n_d}$
AuTe ₂	0.30	-0.6 ₈	-0.1	0.05	0.22	-0.1 ₇	-1.3
Au _{0.052} Te _{0.948}	0.42	-0.6 ₂	-0.2	0.04	0.20	-0.1 ₆	-1.3
AuSb ₂	0.22	-0.5 ₅	-0.5	0.09	0.29	-0.20	-1.5
AuSn ₄	1.10 ^b	-0.9 ₃	-0.5 ₅	0.04	0.30 ^b	-0.26	-1.2
AuSn ₂	1.32	-1.0 ₅	-0.4 ₅	0.02	0.34	-0.32	-1.1
AuSn	0.45 ^b	-0.8 ₁	-0.3 ₅	0.08	0.26 ^b	-0.18	-1.4
Au _{0.099} Sn _{0.901}	1.35	-1.0 ₅	-0.6 ₅	0.04	0.34	-0.30	-1.1
AuIn	0.38	-0.9 ₆	-0.6	0.13	0.31	-0.18	-1.7
AuIn ₂	0.71	-1.2 ₄	-0.8	0.15	0.40	-0.25	-1.6
Au _{0.050} In _{0.950}	0.60	-1.2 ₄	-1.1 ₅	0.20	0.40	-0.20	-2.0
AuCd	0.30	-0.5 ₁	-0.5	0.09	0.17	-0.08	-2.0
AuCd ₃	0.70	-0.7 ₄	-0.7 ₅	0.09	0.28	-0.19	-1.5
Au _{0.050} Cd _{0.950}	0.86	-0.7 ₄	-0.9 ₅	0.09	0.28	-0.19	-1.5
AuGa ₂	1.30 ^c	-1.3	-0.6 ₅	0.07	0.48 ^c	-0.41	-1.2
AuAl ₂	1.35 ^c	-1.9	-0.6	0.13	0.61 ^c	-0.48	-1.3
	1.95 ^d			0.07		-0.54	-1.1
Au _{0.050} Cu _{0.950}	0.50	-1.1 ₂	-0.4 ₅	0.12	0.36	-0.24	-1.5
Au _{0.050} Zn _{0.950}	1.09	-0.9 ₀	-0.8	0.07	0.29	-0.22	-1.3

^a δ values are evaluated according to Eq. (7) given in the text.

^b Reference 2.

^c Reference 1.

^d Reference 25.

ϕ values are from the literature,¹⁷⁻²⁰ and the F 's are calculated.^{1,2} Several factors have not been included in Eqs. (5) and (7). Volume effects, as discussed earlier, are unimportant for the alloys here considered and are neglected. Also of concern is the neglect of change in screening of the final-state $4f$ hole. However, since all the samples are metals and should be approximately equal in screening ability and since we are only interested in the differences of the binding energies, it is reasonable to expect only small quantitative errors to be associated with the neglect of screening differences. Perhaps more important is the uncertainty associated with the approximation of $\Delta\epsilon_F$ by experimentally known $\Delta\phi$ in Eq. (7).

In addition to the ΔE_B values obtained here for Cd-, In-, Sn-, Sb-, and Te-based alloys, those reported previously¹⁻³ for Ga and Al are also included. Work functions of the alloys have been approximated by linear interpolation between the values for the two constituents. The factors $F_c - F_d$ and $\mathcal{E}_{\text{latt}} - F_d$ have been calculated previously to be -3.1 ± 0.3 eV and -9 ± 2 eV, respectively.² Δn_c was obtained from Eq. (4) and Table I. Results of the calculation from Eq. (7) are shown in Table III. It is immediately apparent that all the δ values are quite small, i. e., ~ 0.1 , and that δ values within the same alloy system are similar. The Sn system is somewhat ill behaved; the isomer shifts²¹ and the ΔE_B do not vary monotonically with composition and this is reflected in the δ values, which

are exceptionally small. Detailed study of the relationship between δ and Δn_c is unfortunately restricted by the uncertainties of these values, but the results clearly demonstrate that an $s-d$ compensation mechanism is operating, that is, that Δn_c and Δn_d are opposite in sign, with $\Delta n_c + \Delta n_d$ in the order of $\sim +0.1$ electron. The ratio $\Delta n_c / \Delta n_d$ also shown in Table III, is surprisingly constant, given the various numerical uncertainties of the analysis. This constancy may be a general characteristic of Au in its alloys and perhaps of transition metals¹¹ generally. In Fig. 1(a), the δ values of Table III together with some previously evaluated³ for Pt-, Ag-, Ni-, and Pd-based Au alloys are plotted versus the Pauling electronegativities of the host metals. It appears that there is a qualitative correlation consistent with the overall direction of the charge flow onto the Au site. If there should be an error in the $\Delta\epsilon_F$ values because work functions were used to estimate them, this is expected to be largest in the case of Au; electrochemical arguments suggest that its Fermi level should be placed lower with respect to those of the other elements. A crude estimate shows that this would tend to increase the tabulated δ by a roughly constant $0.05e$.

A plot of Δn_c versus Pauling electronegativity [Fig. 1(b)] correlates better than δ ; this is in part because Δn_c is better determined. It is interesting to note that the electronegativity, which is a measure of $\delta = \Delta n_c + \Delta n_d$ by definition,²² does

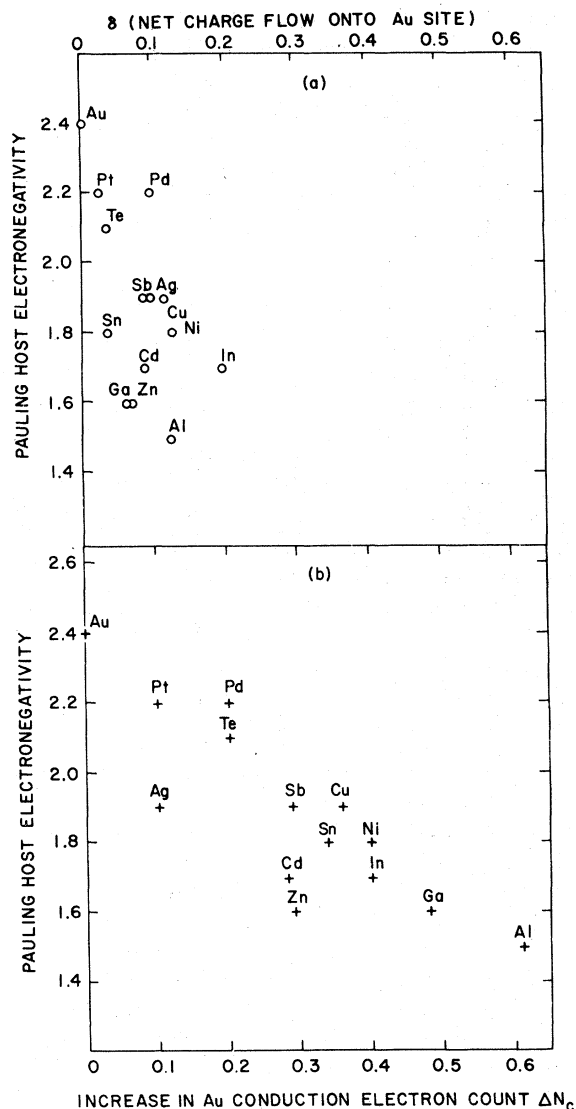


FIG. 1. Pauling electronegativity of the host is plotted against (a) δ the net charge flow onto Au site, and (b) the increase in Au conduction electron count Δn_c . Note that the δ and Δn_c values are drawn according to the same scale.

not correlate with ΔE_B at all. This illustrates the complexity of charge transfer upon alloying; electronegativity scales may describe certain alloy properties nicely but sometimes fail to do so. It is, however, important to realize that the atomic constituents of these alloys tend to maintain electro-neutrality to within ~ 0.1 electron.

VI. VALENCE-BAND SPECTRA

The valence-band spectra for the intermetallic compounds of known structure are shown in Fig. 2. Several interesting features are clearly seen.

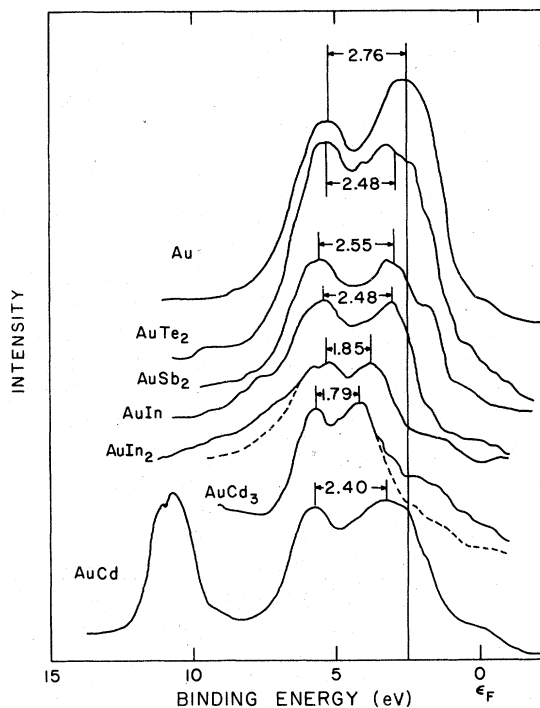


FIG. 2. Valence-band spectra of Au-main-group intermetallic compounds drawn to the same energy scale (eV) but arbitrary intensity. The vertical line aligns the Au spectrum relative to the rest. The dotted lines represent the resultant spectrum after $K\alpha_3$, $K\alpha_4$ contributions to the main-group $4d$ levels are subtracted. The apparent splittings are measured as marked and the doublet at ~ 12 eV in the AuCd spectrum is the $Cd_{4d_{5/2,3/2}}$ level.

(a) All spectra show doublet structure characteristic of the high density of states in the Au $5d$ bands. Increasing dilution of Au in the compounds is associated with shift in doublet position to higher binding energy and decrease in the peak separation. In other words, the position of the first d -band peak (relative to ϵ_F) at lower binding energy is much more sensitive to alloying than the position of the second peak. (b) The d -band components become narrower in the alloys and the relative intensity of the components which derive from the $d_{5/2,3/2}$ doublet, $I_{\text{quasi } 5/2}/I_{\text{quasi } 3/2}$, decreases. These results are consistent with other observations^{2,23-26} of valence-band structure in Au-main-group intermetallics and appear to be general for Au alloys.

Several factors must be considered in connection with these observations: namely, $5d$ spin-orbit effects, intrinsic dilution effects, and finally $5d$ hybridization with $6s$ and covalent mixing with host valence orbitals.

It is commonly recognized that the splitting (~ 2.8 eV) and broadening of the d bands observed

in pure Au is the result of a combination of spin-orbit and band effects since the observed free atom $d_{3/2}$ - $d_{5/2}$ splitting is only 1.5 eV. If Au atoms are physically diluted in a dissimilar host matrix or compound, the atoms are further apart than in the pure metal, and one would expect substantial bandwidth narrowing. Experience suggests that in the absence of spin-orbit splitting this narrowing would be more severe than that seen in Fig. 2. The observed band narrowing and decrease in apparent doublet separation can be understood as a combination of intrinsic dilution, hybridization, and spin-orbit effects. Crystal field effects, which may exist in some noncubic alloys, should be small and should not contribute significantly to the shapes or widths of the d -band structure at the instrumental resolution in these measurements.

The most important phenomenon of all is probably the hybridization of the d bands upon alloying, such as the s - d hybridization or mixing of the s and d orbitals of Au with the s and p orbitals of the main-group atoms. We suggest that in Au intermetallic compounds or dilute alloys because the Au atoms normally do not have like nearest neighbors, d -band width is determined by distant Au-Au interactions through mixing with host orbitals; thus states and virtual orbitals are formed through which some of the d -band electrons can tunnel out, losing part of their d character. This loss of d charge at the electronegative Au sites is compensated by s -like-conduction-electron screening.

Important consequences of this s - d compensation upon alloying should be apparent in the valence-band spectra since, with Al or Mg $K\alpha$ x-ray radiation, only Au $5d$ electrons have large enough cross section to contribute effectively to the intensity. In the absence of countervailing symmetry arguments,²⁷ one expects hybridization effects to be strongest in the d bands closest to the Fermi level and a depletion of intensity at the first d -band peak close to the Fermi level accompanied by a shift of this peak away from the Fermi level. These effects are indeed observed. The shift of the peak near the Fermi level is too large to be consistent with the binding energy shifts of the core levels and must be due to a combination of hybridization effects with those potential energy effects responsible for the core-level shifts.

VII. CONCLUSION

The results reported here are consistent with, and extend previous observations, that Au, in forming alloys and intermetallic compounds with other metals (at least main-group metals), gains electron character concomitant with the loss of $5d$ -electron character, in contradiction to the idea sometimes held that $5d$ character is not greatly involved in the alloying process. This s - d compensation turns out to be a general feature of Au-main-group alloys and the amount of net charge flow δ is estimated to be ~ 0.1 electron onto the atomic Au site. The ratio $\Delta n_e/\Delta n_d$ turns out, within experimental uncertainties, to be surprisingly constant. This behavior may be a general characteristic of Au in its alloys and perhaps even of transition-metal alloys in general.¹¹ The net charge flow correlates with the electronegativity of the hosts. It is interesting to note that the isomer shifts S themselves correlate more closely with electronegativity than do the δ values. Similar charge compensation exists in zero-valent organometallic compounds (e.g., metal carbonyl), where donation and back donation of electrons to and from the central metal is a necessary condition for compound formation. Substantial hybridization of the Au d bands with s and p states of the hosts is observed in the valence-band spectra, which exhibit appreciable decrease of d -band intensity with increasing dilution. The drop in intensity of the d band close to the Fermi level is clearly suggestive of d character depletion. Finally, we report in this paper, for the first time, almost identical isomer shifts for some Au-main-group intermetallic compounds and their dilute alloys, a result which suggests strongly that the local order in each of these dilute alloys is similar to that in the corresponding intermetallic compound and that this similarity is responsible for the observed S correspondence. Further experiments are needed to characterize local environments in dilute alloys.

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