

Electronic Behavior in Alloys: Au-Sn[†]

Robert M. Friedman,* J. Hudis, M. L. Perlman, and R. E. Watson

Brookhaven National Laboratory, Upton, New York 11973

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Charge-flow and valence-*d*-band behavior in Au alloys have been studied in the Au-Sn alloy system by x-ray photoemission measurement of the valence bands and of core-level energy shifts for both atomic species. Published Mössbauer isomer-shift data for these alloys indicate that there is significant valence *s* charge increase at Au sites and a somewhat smaller decrease at Sn sites upon alloying. An analysis, which includes screening in the Coulomb interactions between valence and core electrons and which combines the Mössbauer and core-level photoemission data, has been carried out. The results indicate that there is little net charge flow between Au and Sn, i.e., that the increase of non-*d* conduction-electron count at Au sites is almost entirely compensated for by a decrease in *5d* count; a similar *s-p* compensation occurs at Sn sites. Coulomb screening is important to this analysis and we have applied it to similar results reported by us previously in the AuAg alloy system. Substantial hybridization of the Au *d* bands with the Au "s" and with Sn valence-electron states is exhibited by the valence-band spectra; and the extent of this hybridization with final states above the Fermi level is indicated by the observed depletion in *d* count.

Alloys of the noble metals have been one of the major testing grounds for ideas concerning charge screening in alloys. In the traditional view, the approximately free conduction-band electrons screen impurities, the *d* bands are full, and *d* character has very little or no role in alloying effects. In a published study¹ of the Au-Ag alloy system (henceforth denoted as I), core-level shifts, deduced from x-ray photoemission spectroscopy, were considered together with Au-site Mössbauer isomer-shift data; from this emerged a picture of little net charge flow to or from a Au site but, instead, of a substantial increase in conduction or "s" character compensated by an almost equivalent decrease in *d* character at the site. The question of whether such *s-d* compensation is a general characteristic of Au alloys has been pursued by study of another system. Au_xSn_y was chosen for several reasons. First, Mössbauer isomer-shift data exist^{2,3} for both sites. Second, the molecular volumes of the ordered alloys AuSn and AuSn₄ are almost exactly equal to the sums of the atomic volumes characteristic of metallic Au and white Sn; this provides a natural choice of the atomic volumes attributed to the Au and Sn sites in the sequence of alloys Au_{1.0}Sn_{0.0} → Au_{0.0}Sn_{1.0}. Finally, one wishes to use alloys of Au with a metal having little or no structure in the conduction bands so as to observe the effects of alloying on the Au *d* bands themselves. The information obtained from the *d* band spectra complements that from the core-level shifts. What is more, this information, concerning essentially isolated *d*-band behavior of the one constituent Au, is relevant to that obtained from comparable studies, such as those of Hüfner *et al.*⁴ on Cu-Ni and Ag-Pd, alloys in which the *d* bands of both constituents are separate, close

lying, and interacting.

In this paper the analysis of core-level shifts is taken a step beyond that in I, where bare Coulomb integrals were employed. Relaxation contributions to the Coulomb terms are included here, as they were in a recent study⁵ of white (β) and grey (α) Sn (denoted as II). This analysis shows convincingly that there is almost complete *s-d* compensation and little net charge flow onto Au sites, in both Au_xSn_y and Au_xAg_y.

EXPERIMENT AND RESULTS

Specimens of the pure metals and of the alloys were prepared from pure gold and pure tin⁶ by arc melting under several centimeters pressure of argon in a water-cooled copper crucible. With this method the melts do not wet and are not contaminated by the crucible material. Correct relative amounts of the pure constituents were taken by weight and premelted separately in order to degas them before alloying. Alloy compositions were checked by product weight and by conventional chemical analysis. The final specimen form was a more or less cylindrical slug, about 1 cm diam and 2 cm long.

A Varian IEE-15 photoelectron spectrometer equipped with a Mg x-ray anode was used for the measurement of the core and valence-band electrons. The Au-Sn specimens were cleaned by glow-discharge ion sputtering in 85% Ar-15% H₂ at about 20 mtorr in the isolatable forechamber of this instrument. They were maintained at about -2000 V, and a silica-glass cover sleeve on other negative conductors prevented contamination of specimen surfaces by sputtering from those conductors. Tin electron lines, after specimen cleaning, showed no evidence of oxide impurity.

Photoelectron spectra were measured with the instrument set to transmit 50 eV electrons. For gold the $4f_{5/2,7/2}$ lines and for tin the $3d_{3/2,5/2}$ doublet were the core levels selected. Observed linewidths were ~ 1.1 -eV (Au) and 1.4-eV (Sn) full width at half-maximum (FWHM). There was no evidence of oxide component in the tin spectra and very little O 1s photoline intensity. Data for the core lines are given in Table I. A Rh metal strip in electrical contact with each specimen surface provided energy reference lines for normalization of all Au and Sn core-level measurements to each other. The small binding-energy shifts could thus be accurately determined. Valence spectra were, of course, measured without the Rh foils, and they are shown in Fig. 1. Although these spectra were necessarily obtained without a normalization standard, the stability of the spectrometer is such that their energy scales are not out of register by more than ± 0.1 eV.

ANALYSIS OF RESULTS

Volume Considerations

The atomic volumes in Au and in β -Sn are 17.0 and 27.0 \AA^3 , respectively. The molecular volume⁷ of the ordered compound AuSn is 44.6 \AA^3 , almost exactly the sum of the two pure metal volumes. Similarly, the molecular volume⁷ of AuSn₄ is 121 \AA^3 , while $4V_{\text{Sn}} + V_{\text{Au}}$ equals 125 \AA^3 . The close agreement for both compounds suggests that the pure-metal volumes may properly be used throughout the alloy sequence. Isomer and level energy shifts are thus attributable to changes in the charge character within the volumes rather than to changes in the volumes characteristic of the atomic sites.

Mössbauer Isomer Shifts

Given the required nuclear parameters, an isomer shift is a measure of the difference between the electron charge densities at the nucleus in two chemically or physically different samples. Thus,

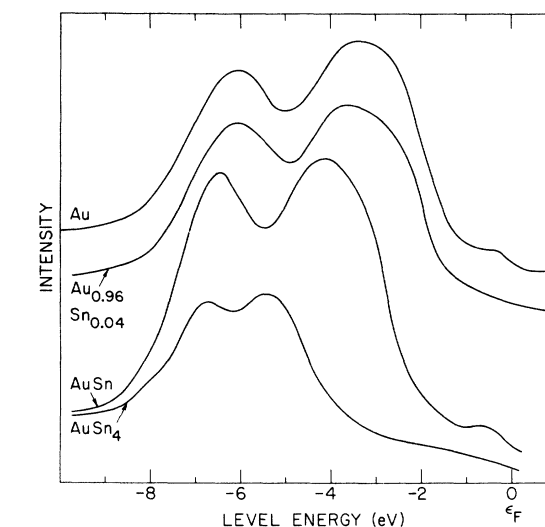


FIG. 1. Valence-band spectra of metallic Au and three Au-Sn alloys. The zero in energy is set at the Fermi level, as described in text. Normalization of the curves is arbitrary.

it provides a measure of the change in the amount of s -like (and relativistic $p_{1/2}$ -like) charge density in the atomic cell surrounding the nucleus in question. For the Au_xSn_y system, the literature² provides

$$S_1 = +3.5 \pm 0.1 \text{ mm/sec for } ^{197}\text{Au in AuSn}_4$$

(absorber relative to an Au absorber),

$$S_2 = -0.57 \pm 0.06 \text{ mm/sec for dilute } ^{119}\text{Sn in Au,}$$

(absorber relative to an AuSn₄ absorber),

$$S_3 = -0.25 \pm 0.07 \text{ mm/sec for } ^{119}\text{Sn in AuSn,}$$

(absorber relative to a β -Sn absorber),

$$S_4 = +3.0 \pm 0.1 \text{ mm/sec for } ^{197}\text{Au in AuSn}$$

(absorber relative to an Au absorber).

TABLE I. Core-level energies of Au and Sn in the Au_xSn_y system.

Sample	Binding energy ($-E$) ^a		Level-energy shift	
	Au $4f_{7/2}$ (eV)	Sn $3d_{5/2}$ (eV)	Δ_{4f} (Au) (eV)	Δ_{3d} (Sn) (eV)
Au	83.40 \pm 0.10		0	
Au _{0.96} Sn _{0.04}	83.50 \pm 0.10	484.60 \pm 0.10	-0.10 \pm 0.14	-0.40 \pm 0.14
AuSn	83.85 \pm 0.10	484.6 \pm 0.10	-0.45 \pm 0.14	-0.4 \pm 0.14
AuSn ₄	84.50 \pm 0.10	484.3 \pm 0.10	-1.10 \pm 0.14	-0.1 \pm 0.14
Sn		484.2 \pm 0.10		0

^aBinding energies are given with respect to the Fermi level, which was located by "Fermi-edge" rise observed at low binding energy in the valence-band spectrum of pure gold. With rise (Fig. 1) set at 0 eV, the $4f_{7/2}$ binding energy in 100% Au is 83.40 eV. The energy of the $3d_{5/2}$ level in 100% Rh, which was used as a reference for the alloy lines, was found to be at -306.8 eV by comparison with the Au $4f_{7/2}$ level.

Conversion of the above data to statements of the changes in conduction-electron count at Sn and Au sites upon alloying must be considered individually for the two species.³ Sn is polyvalent; on the other hand, Au is a one-electron metal with filled *d* bands. Sn is the more straightforward case and will be treated first.

For the free Sn atom, only 8% of the 5*s* charge lies outside the Wigner-Seitz radius r_{ws} , appropriate to β -Sn, as discussed in II. This relatively small spatial extent of the 5*s* shell is due to the polyvalent character of the atom; i.e., the 5*s* is a somewhat interior electron, in a region of effective nuclear charge about $3e$. It may be noted that in metals of the transition *d*'s atoms even more than 8% of free-atom *d* charge extends⁸ beyond the metal radius r_{ws} ; the *d* electrons nevertheless maintain much of their atomic quality. It is thus quite plausible that the valence *s* character in Sn metal is much like the free-atom 5*s*, except for an 8% renormalization⁸ within the atomic cell. Much of the chemistry of Sn is concerned with the relative roles of valence *s* and *p* character, and the above observations suggest the nature of the first term. In this view, the isomer-shift data can be employed to identify quantitatively changes in *s*-electron count on alloying, Δn_s , defined in terms of the renormalized function; and, given this, the core-level shifts, which depend on a sum of *s*- and "*p*"-count changes, can then be used to determine the non-*s* effects, lumped⁹ together as Δn_p .

With the appropriate free-atom contact densities, the Sn isomer shifts can now be converted to Δn_s values if two factors are accounted for. First, there is the above mentioned 8% modification of the contact density due to renormalization. Second, anticipating the alloy results, which will show that most of the change in *s* count within the atomic cell is compensated by an opposing Δn_p , one requires Δn_s for the case in which the atom undergoes a transition $s^x p^y \rightarrow s^{x+\Delta} p^{y-\Delta}$. Employing free-atom Fock-Dirac¹⁰ and relativistic Hartree-Fock-Slater¹¹ calculations, one obtains for the cases of interest

$$\Delta n_s(\text{Sn} \rightarrow \text{AuSn}) = -0.08 \pm 0.02$$

and

$$\Delta n_s(\text{Sn in AuSn}_4 \rightarrow \text{dilute Sn in Au}) = -0.17 \pm 0.02.$$

In contrast with the 5*s* in Sn, the 6*s* electron of a free *d*¹⁰*s* atom of Au lies outermost, having approximately 40% of its charge outside the r_{ws} of Au metal. Distortion of this charge density is substantial on forming the metal and discussion of the isomer shift in terms of a somewhat modified free-atom-like *s* orbital does not seem profitable. What is more, the natural division for a discussion of Au alloying is between *d* and non-*d* effects; therefore

one wishes to employ the isomer-shift data to estimate a count change Δn_c in terms of some suitable average conduction-electron character. In the absence of a detailed description of a particular alloying process, a plausible choice for this average character is that of the Fermi-level conduction electrons. The charge-contact density of these electrons may be related to the free-atom 6*s* by comparison of the Knight shift to the free *d*¹⁰*s* atom magnetic hyperfine constants, i.e., the familiar¹²

$$\xi \equiv \mathcal{K} \mu_B / H_{\text{eff}} \chi_p, \quad (1)$$

where \mathcal{K} , μ_B , H_{eff} , and χ_p are the Knight shift, the Bohr magneton, the free-atom hyperfine field, and the Pauli susceptibility of the metal, respectively. Although electron polarization processes cause magnetic and charge-contact densities to differ substantially, it is nonetheless likely that the ratio ξ provides a usable, albeit crude, measure of the ratio appropriate to the charge density. Matters are further complicated by uncertainty in the value of χ_p for Au and by the fact that one requires a ξ for Fermi-level conduction-band states without contamination by *d* hybridization and hence such hybridization must be estimated and its effect subtracted from \mathcal{K} . A reasonable estimate based on data from the literature¹² is $\xi \approx 0.6$.

Again, anticipating the alloy results, one wishes to estimate Δn_c values for the cases in which the atom remains essentially neutral in charge, i.e., $d^n c^x \rightarrow d^{n-\Delta} c^{x+\Delta}$. This has been done employing free-atom calculations^{10,11} and, with a ξ of 0.6, the results are

$$\Delta n_c(\text{Au} \rightarrow \text{AuSn}_4) = +0.3 \pm 0.1,$$

and

$$\Delta n_c(\text{Au} \rightarrow \text{AuSn}) = +0.26 \pm 0.1,$$

where the uncertainties derive mainly from that of ξ .

Valence-Band Spectra

Valence-band photoelectron spectra are plotted in Fig. 1 for those samples containing Au. The Fermi level is set at the midpoint of the small "Fermi-edge" rise at low binding energy in the curve for pure Au, and the energy scales for the several spectra are correctly located relative to each other to within ± 0.1 eV. It is surprising that the Fermi edge for $\text{Au}_{0.98}\text{Sn}_{0.04}$ does not appear even though it is seen in the spectra of 100% Au and of AuSn. Whether this is due to some artifact of the experiment or to an inherent property of $\text{Au}_{0.98}\text{Sn}_{0.04}$ is not clear.

The intense double-peaked structure common to all the spectra is ascribed to components in the density of states which are essentially of Au 5*d* character. This *d*-band structure narrows and

moves farther below ϵ_F as the Sn concentration increases. There is also a suggestion of a progressive change in shape of the structure, notably the gradual dropping off of the high-energy (low-binding-energy) side of the twin peak seen most clearly in AuSn₄.

Three factors must be considered in connection with the bandwidth narrowing: namely, $5d$ spin-orbit effects, $5d$ hybridization, and intrinsic dilution effects on the $5d$ band.

If the bandwidth is not substantially determined by spin-orbit effects, this third factor, taken alone, leads to narrowing of the d bands as the distance between Au sites increases. For example, in a nearest-neighbor tight-binding scheme for a disordered alloy, the bandwidth varies as the square root of the number of like nearest neighbors.¹³ In an ordered compound the bandwidth varies as the number of like nearest neighbors; and when there are none, any bandwidth arises from more-distant-neighbor interactions. If such intrinsic effects were dominant, one would expect more severe bandwidth narrowing in the case of the ordered AuSn₄ than that observed; the width for this alloy is one-half to two-thirds that for pure Au. This discrepancy is largely due to spin-orbit effects.

A second phenomenon which results in modification of the double peaked d structure is the hybridization of those conduction electrons residing primarily on Sn sites with the Au-site d -band electrons. (Of course, any modification of Au-site s - d hybridization is included.) One such modification possible would be the addition of shoulders to the sides of the d peaks. There is some suggestion that such an effect is present on the high-energy side of the AuSn₄ spectrum. High-energy hybridization shoulders may be a characteristic of many Au intermetallic compounds. Evidence suggesting such a shoulder in AuAl₂ has been presented,¹⁴ and it may be responsible for that metal's mauve (!) color. Additional implications of d band hybridization will be mentioned below.

The doublet structure observed in the valence-band spectrum of pure Au is the result of a combination of spin-orbit and band effects. The $N_{6,7}$ x-ray emission spectrum has been explained¹⁵ on the basis that the wave-function character associated with the lower component of the density of states doublet is largely $d_{3/2}$, and that of the upper component $d_{5/2}$. While this may be true, the observed doublet separation of 2.5–3 eV in pure Au is significantly larger than the observed free d^9s^2 atom $d_{3/2}$ - $d_{5/2}$ splitting of 1.5 eV, a fact which points to the importance of band effects. In AuSn₄ the doublet separation approximately equals the atomic splitting, and it would appear that the spin-orbit splitting is inhibiting the further band nar-

rowing which would otherwise result from the increasing distance between Au sites. Some reduction in spin-orbit splitting is expected to occur on going from Au to AuSn₄: although alloying should not produce as much as 5% modification of the d spin-orbit interaction, which is localized at the Au site, any hybridization of the Au d states with the Au conduction and the Sn s - p valence bands should reduce the sampling of the interaction and hence lead to a reduced splitting. The spectra show no clear indication of this effect. Though the twin-peak region is associated with states which are still predominantly $5d$ in character, other structure, such as the high-energy slope in AuSn₄, is introduced on alloying and there are $5d$ components admixed into the conduction bands above and below ϵ_F . The $5d$ -electron count at a Au site is the sum of all $5d$ weights in states below ϵ_F . Without d hybridization, there would be 10 d electrons in the Au site d bands. Hybridization with states above ϵ_F reduces this count, and the core-level shifts will be employed in the next section to estimate this d depletion.

In addition to becoming narrower, the twin-peak structure falls increasingly far below ϵ_F with alloying. The Au core-electron levels do the same (see Table I). Accurate assessment of the motion of the $5d$ structure is difficult because of its changing shape, but it is surely greater than the 1.05-eV shift measured for the $4f$ -core level on going from Au to AuSn₄. As was discussed in I (see Fig. 1 there), this is the opposite of what would be anticipated if the $5d$ -electron shifts, like those of the $4f$ core, were measures only of changes in the Au site potential. This is so because any change in the Coulomb potential of the site is expected to be more severe in the interior of the ion. Of course, the $5d$ electrons are actively involved with the alloying process. To whatever extent d hybridization involves mixing with valence states lying higher in energy, the d bands are lowered. Unpublished results for the valence bands in the Au_xAg_y system show a similar tendency.

Core-Level Shifts

As was discussed in I, the wave function of a core electron is affected very little by change of the atom's environment; but, because the potential in the core region changes, there is a change in the electron energy. For the case in which atomic volumes are fixed, as in the Au_xSn_y system, the spherical Coulomb energy shift sustained by a core electron i is

$$\begin{aligned} \Delta\epsilon_i &= \int [\rho_i(r_1) \times \Delta V(r_1)] r_1^2 dr_1 \\ &= \int [\rho_i(r_1) \times \Delta \int (1/r_2) \rho(r_2) r_2^2 dr_2] r_1^2 dr_1, \quad (2) \end{aligned}$$

where the inner integral accounts for any change

of the valence electron distribution within the atomic cell plus any change in the contributions from the charge outside. Aspherical and exchange terms are smaller than the uncertainties which will be encountered and will be neglected.

Attributing the change of charge distribution to changes in the count of various types of valence electrons, Eq. (2) may be rewritten

$$\Delta\epsilon_i = \sum_j^{\text{val}} [\Delta n_j F^0(ij)] - \left[\sum_j^{\text{val}} \Delta n_j \right] F_{\text{latt}}^0. \quad (3)$$

Here the F^0 's are Coulomb interaction terms, and Δn_j is the change in valence electron j count. The first term gives the energy change produced by effects on the parent atom and the second term is associated with the charge changes on the other lattice sites due to the charge flow

$$\delta = \sum_j^{\text{val}} \Delta n_j \quad (4)$$

into or out of the parent atomic site. For Au with its d and conduction-electron terms and for Sn with its s and " p " the above may be specialized to

$$\Delta\epsilon_i(\text{Sn}) = \Delta n_s [F^0(i, s) - F^0(i, p)] + \delta_{\text{Sn}} [F^0(i, p) - F_{\text{latt}}^0]. \quad (5)$$

and

$$\Delta\epsilon_i(\text{Au}) = \Delta n_c [F^0(i, c) - F^0(i, d)] + \delta_{\text{Au}} [F^0(i, d) - F_{\text{latt}}^0]. \quad (6)$$

In these expressions the Coulomb contributions are grouped in terms of Δn_s and Δn_c values inferred from the Mössbauer isomer-shift data and in terms of the net charge flows, δ 's, which prove to be small. The lattice terms in the two expressions are, of course, different. If valence-electron orbitals within the cells are frozen, the valence-electron terms become the familiar Slater integral

$$F^0(i, j) - F_{\text{latt}}^0(i, j) \equiv \int \int P_i(r_1)^2 (1/r_{12}) P_j(r_2)^2 dr_1 dr_2, \quad (7)$$

where the $P(r)$ are one-electron radial functions normalized such that $\int P(r)^2 dr = 1$. For example,¹⁶ in the case of a renormalized $5d^{10}6s$ Au site

$$F_{\text{latt}}^0(4f, 5d) = 1.61 \text{ Ry}$$

and

$$F_{\text{latt}}^0(4f, c) = 1.06 \text{ Ry};$$

for a renormalized $5s^2 5p^2$ Sn site

$$F_{\text{latt}}^0(3d, 5s) = 1.11 \text{ Ry}$$

and

$$F_{\text{latt}}^0(3d, 5p) = 0.97 \text{ Ry}.$$

Bare integrals such as these were used in I. However, they do not account for the relaxation of the valence shells on the removal or addition of charge. This can be done by use of effective Coulomb terms such as

$$F^0(4f, 5d) = \left(\sum F^0(4f, v) \right)_{d^{n_c x}} - \left(\sum F^0(4f, v) \right)_{d^{n-1, c^x}} \quad (8)$$

for the removal of a d electron from a Au site.

The sums span all valence (v) electrons, conduction as well as d , the first set of large parentheses involving wave functions for the renormalized $d^n c^x$ configuration, the second for the configuration with one fewer d electrons. A sample of various pairs of configurations in which the pair members differ by one "valence" electron results in the terms

$$F^0(4f, 5d) = 1.19 \text{ Ry}$$

and

$$F^0(4f, c) = 0.95 \text{ Ry},$$

for Sn

$$F^0(3d, 5s) = 1.00 \text{ Ry}$$

and

$$F^0(3d, 5p) = 0.88 \text{ Ry}.$$

The d shell $F^0(4f, 5d)$ for Au is the most substantially screened or relaxation affected of these parameters, the first set of brackets of Eq. (6) being reduced to 40% of the bare Slater integral value. This behavior, characteristic of the transition metals as well as the noble metals, must be recognized in the analysis of core-level shifts.

Two additional factors must be taken into account before Eqs. (5) and (6) can be related to the measured shifts given in Table I. First, Eqs. (5) and (6) provide estimates of the chemical shifts of the Hartree-Fock one-electron energies. In general, however, the position of the main core-level photoemission peak does not furnish a direct measure of this one-electron energy; Meldner and Perez¹⁷ and others¹⁸ have shown that, due to final-state relaxation effects, it is the center of gravity of the main line with its satellites, if any, which corresponds to the one-electron energy. This statement is rigorous when the initial state is describable as a single determinant. Inasmuch as there were no discernible changes in the Au $4f$ and Sn $3d$ satellite structures, it will be presumed that the *shifts* in peak position to be inferred from Table I are accurate measures of the *shifts* in centers of gravity appropriate to Eqs. (9) and (10) below. Second, the Fermi level ϵ_F of the sample, which is in me-

tallic contact with the spectrometer, is brought to that of the instrument.¹⁹ Now the one-electron energy shifts of Eqs. (2), (3), (5), and (6) are calculated with respect to a zero of the potential within the crystal and not with respect to ϵ_F . Therefore any shift in ϵ_F with respect to the chosen zero must be accounted for when relating the experimental energy level shifts Δ to the $\Delta\epsilon_i$. On going from alloy X to alloy Y , as indicated in Fig. 2, we have

$$\begin{aligned} \Delta_i(X \rightarrow Y) &= E_i^Y - E_i^X = (\epsilon_i^Y - \epsilon_i^X) - (\epsilon_F^Y - \epsilon_F^X) \\ &= \Delta\epsilon_i - \Delta\epsilon_F(X \rightarrow Y). \end{aligned} \quad (9)$$

The observed level shift for Sn is thus

$$\begin{aligned} \Delta_{3d}(X \rightarrow Y) &= -\Delta\epsilon_F(X \rightarrow Y) \\ &+ \Delta n_s [F^0(3d, s) - F^0(3d, p)] \\ &+ \delta_{Sn} [F^0(3p, d) - F_{latt}^0], \end{aligned} \quad (10)$$

and for Au on going from alloy (or pure metal) X' to Y'

$$\begin{aligned} \Delta_{4f}(X' \rightarrow Y') &= -\Delta\epsilon_F(X' \rightarrow Y') \\ &+ \Delta n_c [F^0(4f, c) - F^0(4f, d)] \\ &+ \delta_{Au} [F^0(4f, d) - F_{latt}^0]. \end{aligned} \quad (11)$$

The one-electron energy shifts $\Delta\epsilon_i$ of Eqs. (2), (3), (5), (6), and (9) are calculated in terms of ϵ_i 's with respect to an effective vacuum zero. This zero would be the vacuum zero except that it does not include the metal-surface-potential contributions. Thus no variation in such surface-potential contributions should enter the values of the $\Delta\epsilon_F$'s. Ex-

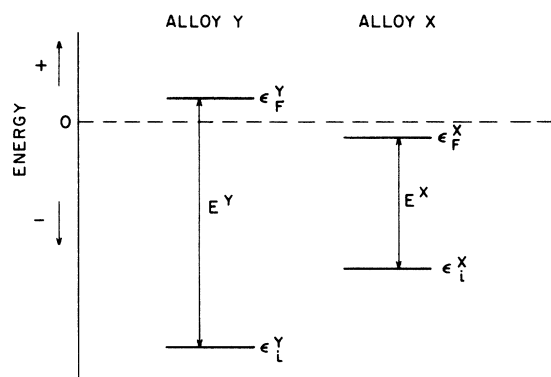


FIG. 2. Level diagram for a given atomic species in two different alloys, X and Y . By photoelectron spectroscopy one measures a given level i at energies E^X and E^Y below the respective alloy Fermi levels ϵ_F^X and ϵ_F^Y . Model calculations of the chemical shift place the levels at ϵ_i^X and ϵ_i^Y with respect to some zero of potential within the crystal (chosen for computational convenience). This zero is used as the origin in the diagram and the Fermi levels must be placed with respect to it if the model calculations are to be related to experiment.

perimental work functions Φ include such contributions and hence cannot be used, without correction, to estimate the $\Delta\epsilon_F$. In addition, the Φ themselves are poorly determined. Estimation of $\Delta\epsilon_F$ values sufficiently accurate for use in Eqs. (10) and (11) is extremely difficult, and one would prefer to treat $\Delta\epsilon_F$ as one of the unknowns to be determined by solution of the equations.

Perhaps the simplest alloying case to consider is that of pure Au and pure Sn being combined into the 50-50 compound AuSn; here

$$\delta_{Au-AuSn} = -\delta_{Sn-AuSn}.$$

Unfortunately, no such simple relation occurs between the Fermi-level shifts; but, if one assumes that ϵ_F varies monotonically across the alloy sequence and notes the trends in the data for Δ and the isomer shifts, one has

$$\Delta\epsilon_F(Au \rightarrow AuSn) = -\xi \Delta\epsilon_F(Sn \rightarrow AuSn),$$

where

$$\xi = 0.8 \pm 0.2.$$

If one assumes further that the lattice terms are equal to or somewhat smaller than the Coulomb interaction which would correspond to the displaced charge δ being located on the surfaces of the respective Sn and Au atomic spheres, one obtains

$$F_{latt}^0 = 7 \pm 2 \text{ eV} \quad \text{and} \quad \mathfrak{F}_{latt}^0 = 6 \pm 1 \text{ eV},$$

the latter smaller since the Sn radius is larger. With these assumptions, the Δn_c and Δn_s values and the level-shift data, Eqs. (10) and (11), yield

$$\delta_{Au-AuSn} = +0.04 \pm 0.09 = -\delta_{Sn-AuSn} \quad (12)$$

and

$$\Delta\epsilon_F(Sn \rightarrow AuSn) = +0.3 \mp 0.6 \text{ eV}. \quad (13)$$

The uncertainties are coupled so that a more negative δ is associated with a more positive $\Delta\epsilon_F$ and vice versa; the signs imply charge flow onto the Au site and a Sn Fermi level which is lower than that of Au. Au is traditionally thought of as the most electronegative of metals, attracting charge to its site in an alloy and presumably having the lower ϵ_F with respect to the zero of Eqs. (10) and (11). The work function of Au is 0 to 1 eV greater²⁰ than that of Sn and thus, if there were no difference in surface potential, this would imply that the Au Fermi level is lower than that of Sn by 0 to 1 eV, opposite to what is obtained above [Eq. (13)]. According to the model theory of Lang and Kohn,²¹ the surface potential is greater in Sn than Au, and this, if true, implies that the Au ϵ_F lies still lower with respect to the Sn level. It may be noted, however, that the Lang-Kohn electron-gas work-function model gives a mediocre result for gold. According to this model the work function of Au arises

from one free electron per atom and d electrons make no contribution whatsoever; for Sn, having four free electrons per atom, the theoretical value for the work function is in reasonable accord with experiment.

A reasonable conclusion from Eqs. (12) and (13), in the context of the discussion above, is that in AuSn there is little change in Fermi level and little charge flow relative to the Au site Δn_c of +0.26.

Numerically useful results may be had from the alternate case in which the Fermi-level shifts, but not the δ , are common to Eqs. (10) and (11). This situation is approached for the pairs AuSn₄-Au for Au shift and AuSn₄-Au_{0.96}Sn_{0.04} for Sn shift. Here, the equations yield

$$\delta_{\text{Au}}(\text{Au} \rightarrow \text{AuSn}_4) = -0.01 \pm 0.04 + \frac{\Delta\epsilon_F(\text{Au} \rightarrow \text{AuSn}_4)}{F^0(4f, 5d) - F_{\text{latt}}^0} \\ \approx +\Delta\epsilon_F/(9 \pm 2) \quad (14)$$

and

$$\delta_{\text{Sn}}(\text{AuSn}_4 \rightarrow \text{“dilute” Sn in Au}) \\ = -0.004 \pm 0.02 - \frac{\Delta\epsilon_F(\text{Au} \rightarrow \text{AuSn}_4)}{F^0(3d, 5p) - F_{\text{latt}}^0} \\ \approx -\Delta\epsilon_F/(6 \pm 1). \quad (15)$$

Thus, except for the Fermi-level shift, the δ 's are seen to be essentially zero, a result of the near equality of the Δ and the Δn_c (and Δn_s) terms of Eqs. (10) and (11). From the earlier discussion it would seem that $\Delta\epsilon_F(\text{Au} \rightarrow \text{AuSn}_4)$ is small and, most likely, positive, at most +1 eV. Such a value would imply $\delta_{\text{Au}} \leq +0.1e$, substantially smaller than the Δn_c value of +0.30. The δ_{Sn} is opposite in sign and somewhat larger relative to its Δn_s of -0.17.

Uncertainties in the experimental and theoretical parameters make Eqs. (14) and (15) sufficiently ill conditioned that one cannot usefully relate the δ 's by charge conservation. The F_{latt} values are the most crudely estimated of the parameters (initially, one had rather hoped to learn something of them from experiment). Since they enter only in terms multiplying δ of Eqs. (10) and (11) and since they cannot be larger than the $F^0(d)$ and $F^0(p)$, their uncertainties have a moderate effect on the magnitude of the δ 's but no effect on the signs.

AuAg and AuAl₂ Revisited

For the analysis in I of data for the AuAg system, unscreened values for the Coulomb terms were used. It seems appropriate here to consider the effect of a change to screened values in the sense of Eq. (8). One then obtains

$$\delta_{\text{Au}}(\text{Au} \rightarrow \text{AuAg}) = +0.02 + \frac{\Delta\epsilon_F(\text{Au} \rightarrow \text{AuAg})}{9 \pm 2}.$$

The s - d compensation is even more important than it was deduced²² to be in I; and, if the Fermi-level shift is small, the compensation in fact is nearly complete relative to the Δn_c value of +0.13.

AuAl₂ was also studied in I, and here also the use of Coulomb terms which include screening effects leads to more nearly complete s - d compensation.

SUMMARY AND CONCLUSIONS

Isomer-shift (IS) data and valence-band and core-level photoelectron spectra of the Au_xSn_y alloy system are considered in this paper. The isomer-shift data have been treated somewhat differently for the two atomic species due to differences in their valence electron character. The IS data for Sn have been used as a direct measure of the change in count Δn_s of what are essentially atomic 5s valence electrons; the IS data for Au have been combined with other information to obtain the change Δn_c in non- d -band conduction-electron count. These Δn 's are then employed in the analysis of the total charge flowing onto or off the atomic sites. It is assumed, in the analysis, that the Au conduction-electron character remains fixed over the alloy range.

The valence-band spectra display a double Au 5d-band peak, which drops lower in energy relative to ϵ_F and becomes narrower²³ as the Au becomes more dilute. This narrowing, attributed to the effects of increasing Au-Au separation, appears to be inhibited by the intrinsic $d_{3/2}$ - $d_{5/2}$ spin-orbit splitting. Some reduction in spin-orbit splitting due to Au d -Sn site hybridization is anticipated, but evidence for it cannot be seen in the data. There does not appear to be hybridization on the scale suggested by Pauling's assignment²⁴ of a formal valence $\sim 5\frac{1}{2}$ to Au. Most of the hybridization of d character out of the twin-peak region should be into occupied states, i.e., states below ϵ_F , and such mixing does not affect the total d count.

The core-level energy shifts with the isomer-shift estimate of Δn_c are employed to estimate both the total charge flow onto or off of a Au site and the decrease in d -electron count due to increasing d hybridization with states above ϵ_F . The Au_xSn_y and Au_xAg_y results suggest that almost no charge flows into or out of a Au site upon alloying. This means that the d -count depletion Δn_d is just about equal to $-\Delta n_c$; the s - d compensation seems more nearly complete than was inferred in I. The d depletion is of the order of a few tenths of an electron, less than what might be suggested by casual inspection of the valence-band spectra. These spectra are actually consistent with small Δn_c ; because the peak region lies well below ϵ_F there should be only little admixture to states above it.

The isomer-shift data, which date back 10

years and which give evidence for conduction-electron charge flow onto Au sites upon alloying, have seemed consistent with the view that Au is strongly electronegative. One now sees that charge neutrality, i. e., the principle of "minimum polarity," is maintained to a marked degree in these alloy systems. The supposed strong electronegativity of Au, as manifested by conduction electron flow onto it, would seem to be just the screening of the d charge depletion due to hybridization.

Relative to white tin, Sn sites in the Au alloys have increased p and reduced s character. The results suggest that the s - p compensation in Sn is

less complete than the s - d effect in Au.

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*Present address: Institut des Sciences de la Terre, Université Catholique de Louvain, 3030 Heverlee, Belgium.

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¹⁶These integrals were evaluated with wave functions obtained from a relativistic Hartree-Fock-Slater program. When necessary, appropriate averages were taken over the spin-orbit split subshells (e.g., the $d_{5/2}$ and $d_{3/2}$ of Au). Experience (Ref. 8) with the lighter transition metals suggests that the renormalized $6s$ shell of Au is not a bad approximation to some average radial density in the Au conduction band and it has been employed in $F^0(4f, c)$. Similarly, the $F^0(3d, 5p)$ has been used to represent the non- s component of the Sn valence density.

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²²The Δn_c and n_d of I have been used by C. D. Gelatt and H. Ehrenreich [Bull. Am. Phys. Soc. **18**, 93 (1973)] in a coherent potential approximation calculation for the Au_xAg_y alloy system. The fact that we report a new value for Δn_d ($\Delta n_d = \delta - \Delta n_c$) does not invalidate their calculation, because they require the product of Δn and a Coulomb, F^0 , term, which product holds approximately constant.

²³Kapoor *et al.* (Ref. 14) have noted a similar reduction (on the scale of the AuSn result) in the Au- d -band peak splitting in the Au_xAl_y alloy system and have attributed it to bonding and to a "large amount of electron transfer" from Au to Al. As indicated in I, the combined isomer- and core-level-shift data indicate a small net flow of charge in the opposite direction for $AuAl_2$.

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