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Charge transfer in CsCl-structure intermetallic compounds

G. K. Wertheim, R. L. Cohen, G. Crecelius,* K. W. West, and J. H. Wernick
Bell Laboratories, Murray Hill, New Jersey 07974

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Core-electron binding-energy shifts of CuZn, AgCd, AuZn, and AuMg, and Mössbauer-effect ^{197}Au isomer shifts of AuZn, AuMg, AuRb, and AuCs are presented. X-ray-photoemission valence-band spectra are interpreted as showing that there is a tendency to fill the *d* states of metallic gold when compounds are formed with Zn, Mg, and Cs. A consistent interpretation of the charge transfer on alloy formation is obtained by postulating charge flow from states with 6*p* character in Au metal to 5*d* and 6*s* states in the intermetallic compounds.

I. INTRODUCTION

A recent study of the thermochemical properties of CsCl-structure intermetallic compounds[1] demonstrated well-defined systematics as well as certain anomalies which prompt further investigation of these materials. Of special interest is the compound AuMg which has a melting point well outside of the trend of the systematics. We have examined a series of isostructural noble-metal compounds using x-ray-photoelectron spectroscopy (XPS) core- and valence-band spectra, and where applicable, the Mössbauer-effect isomer shifts, to determine the charge transfer which accompanies alloy formation.

Although the difficulty of evaluating charge transfer from XPS binding-energy shifts is not to be minimized, the measurements and supporting calculations presented here show that a substantial fraction of one full electron can be transferred to the gold in Au*X* compounds when the Au-*X* electronegativity difference is large. This conclusion is bolstered by the XPS valence-band spectra, which show that as the Au-*X* electronegativity difference increases, the gold 5*d* states approach atomic 5d^{10} character. This finding contradicts models which require back-transfer of 5*d* electrons to maintain electroneutrality of the gold.

Charge transfer affects the binding energy of core electrons by virtue of the Coulomb potential produced within the atom by the gain or loss of charge by outer orbitals. XPS binding energies are, however, a property of the hole state produced by removal of the core electron. They are strongly influenced by the final-state relaxation and screening response of the solid to the formation of the core hole. Since the extra-atomic relaxation may well be affected by alloying, it must be included in a complete formulation of the problem.

We draw on earlier analyses[2–6] to express the core-electron binding-energy (CEBE) shift, δE_i, resulting from alloy formation in terms of four major contributions

$$\delta E_i = \sum_j F(i,j)\,\delta z_j - M\delta z - \delta R - e\,\delta\phi \quad . \qquad (1)$$

The first term describes the Coulombic effect on an electron in the *i*th shell by charge δz_j added to the *j*th valence shell. $F(i,j)$ is a Coulomb integral, generally of the order of 1 Ry, and often taken to be inversely proportional to the atomic radius. M is the Madelung potential due to the charges on the other atomic sites, δR is the change in final-state relaxation energy from metal to alloy, and $\delta\phi$ is the change in Fermi energy on alloy formation. Note that charge transfer is an *initial*-state effect, while relaxation is a *final*-state effect peculiar to the photoemission process. The interplay between these two phenomena is crucial to the proper interpretation of CEBE shifts.

The summation in Eq. (1) generally contains only a small number of terms, involving outer *s*, *p*, and *d* orbitals. The values of F for a deep core level are usually not a strong function of the nature of the added charge. For example, in Sn, $F(3d,5s)$ and $F(3d,5p)$ differ by only 12%, and even in Au $F(4f,c)$ and $F(4f,5d)$ are of comparable magnitude, 0.95 and 1.19 Ry, respectively.[4] If one is satisfied to calculate only the net charge transfer, δz, it is then reasonable to replace the summation by $F\delta z$, where F is an effective average Coulomb integral.

In an equiatomic *AB* alloy we can write an Eq. (1) for each constituent and make use of the conservation of charge to eliminate the generally unknown Fermi level of the alloy to obtain

$$\delta z_A = -\,\delta z_B = \frac{\delta E_A - \delta E_B - e(\phi_A - \phi_B) + \delta R_A - \delta R_B}{F_A - M_A + F_B - M_B} \quad , \qquad (2)$$

where ϕ_A and ϕ_B are the work functions of the *pure constituents*. The work function of the *alloy* can be computed from

$$e\phi = e\phi_A - \delta E_A - \delta R_A + (F_A - M_A)\delta z_A \tag{3}$$

to provide a check on the methodology. (The generalization of these equations for A_xB_{1-x} alloys or even to ternary systems presents no difficulty.)

Application of these equations encounters a number of problems. The first arises from a substantial cancellation between the poorly known values of F and M. The values of F were estimated by scaling the calculated $F(4f,c)$ for Au inversely with atomic radius. For the ordered CsCl-structure compounds M was calculated as the Madelung potential due to point charges at the lattice sites. (In disordered alloys it should be substantially reduced.) Comparisons between δz's calculated using consistent estimates of F should be meaningful, even though the δz may have large error limits.

The second problem arises from the relaxation energy which is also not known with high accuracy. Some information on R has emerged from recent studies of CEBE shift in the formation of the metal from free atoms.[7–11] The reduction in CEBE due to screening in the metal is generally in the range from 2 to 8 eV. For the present study we need the difference between the relaxation energies appropriate for the formation of the alloy and the constituent metals. One can argue that since the screening takes place on an atom which is impuritylike by virtue of its core hole, only the empty orbitals of the atom itself are relevant for the screening process. δR should then remain small for atoms which form metals and alloys with *sp* conduction bands. δR should become important when the nature of the screening charge changes from metal to alloy, especially if the metal has a partially filled *d* band which becomes filled in the alloy. The behavior of the relaxation energy in transition-metal intermetallic compound in which the *d* bands are strongly modified by alloying is, in general, not predictable. (For screening by a single band, a Thomas-Fermi formulation shows that the relaxation energy varies as the square root of the density of states.)

In the calculation we have used tabulated photoelectric work functions[12–14] without making a correction for the surface dipole term.[3,4] Unfortunately the values quoted in the literature vary between wide limits. Where available we have used the results of recent work with clean surfaces.[14]

II. EXPERIMENTAL

The AuMg, AuZn, and AgCd alloys for these experiments were prepared by standard metallurgical techniques. For the XPS experiments the surfaces were cleaned by removing a macroscopic layer with a tungsten carbide blade in 10^{-7} Pa vacuum in a preparation chamber attached to a Hewlett-Packard 5950*A* spectrometer. All measurements were referenced to the experimentally determined Fermi edge of the metal or alloy under investigation. The AuMg and AuZn Mössbauer absorbers were 0.2-mm-thick slices from the same material used in the XPS experiments.

For the Mössbauer experiments the AuCs and AuRb were prepared by loading stoichiometric amounts of Au and high-purity Cs or Rb into a quartz ampule in a nitrogen-filled dry box, evacuating and sealing the capsule, and then heating for 10 minutes at 612 °C for AuCs and 15 minutes at 500 °C for AuRb; these temperatures are just above the melting points of the intermetallics.[15] The ampules were opened in the dry box, and the material was ground in a mortar, sealed with silicone grease into plastic holders, and immediately immersed in liquid nitrogen. The samples were maintained at liquid-nitrogen temperature or below throughout the measurements because they are otherwise rapidly oxidized when in contact with air. The absorbers contained 135 mg/cm^2 of Au.

Attempts to make the Cs and Rb compounds by solid-state reaction at 400 °C were unsuccessful. The Mössbauer spectra showed lines from other phases. In the case of the AuCs, a strong line was found at 4.18 mm/sec (vs Au:Pt); this could only arise from an intermetallic (probably Au_2Cs) which does not appear in the equilibrium phase diagram or in other analyses of the metallurgy of this system. The existence of this new phase must be taken into account in studies involving the Au-Cs system. Samples of AuRb made by solid-state reaction also showed lines due to other phases, but the Au-Rb phase diagram[15] is so complicated that this is not a surprising result. All of the samples were measured at 4.2 K using a standard Mössbauer spectrometer which has already been described,[16] and a source of Au:Pt made by neutron irradiation of enriched ^{196}Pt.

III. RESULTS: XPS MEASUREMENTS

AgCd: The equiatomic AgCd alloy can be prepared both in the ordered CsCl structure and in the disordered bcc phase.[15] Although mechanical cleaning may tend to disorder ductile materials, an earlier study showed significant differences between the valence-band region of the two phases after similar surface preparation.[17] Since the *d* bands of both constituents lie well below E_F in both the pure metals and the alloys, screening involves largely the *sp* bands. On the basis of the above arguments the relaxation correction in this system should be small. Using the numerical data given in Table I we obtain a charge transfer to Ag of 0.02 ± 0.05. The value is

TABLE I. Core-electron binding-energy shifts obtained from XPS data, and input parameters used in the calculation of charge transfer from Eq. (2). The shifts are obtained from the $2p$ levels of Mg, Cu, and Zn, the $3d$ levels of Ag and Cd, and the $4f$ levels of Au.

AB alloy	$\phi_A - \phi_B$ (V)	D[a] (eV)	δE_A (eV)	δE_B (eV)	$\delta R_A - \delta R_B$ (eV)	δz_A[b]
CuZn[c]	0.3	8.9	0.3	−0.2	−0.9	(−0.075)
AgCd	0.3	7.6	0.48	−0.03	~0	0.02 ± 0.05
AgCd disordered	0.3	>7.6	0.33	−0.05	~0	0.00 ± 0.05
AuZn	0.8	8.0	0.54	0.15	(−1.2)	−0.25 ± 0.05
AuMg	1.4	7.7	0.75	0.25	−1.2	−0.4 ± 0.1
AuCs[d]	...	...	...	...	...	−0.7 ± 0.1

[a] $D = F_A + F_B - M_A - M_B$

[b] Negative sign indicates gain of electrons.

[c] Data from Ref. 18.

[d] From Ref. 24.

small because of a close cancellation of the terms in the numerator of Eq. (2). The error is relatively large because of a large range in values for the work function of Ag. The measured CEBE shifts arise almost exclusively from the change in Fermi level on alloy formation; see Table I.

In the disordered alloy the core-electron lines are not appreciably broadened, and the CEB's change only slightly making $\delta z = 0.00 \pm 0.05$. Both observations provide a model-independent confirmation that the charge contrast in this alloy is small. Line broadening would arise from the Coulombic interaction with the random near-neighbor environment in a disordered alloy with appreciable charge contrast. CEBE shifts would arise from a change in the Madelung potential with disorder. Of course, the fact that AgCd is readily prepared in the disordered phase is itself an indication that the charge transfer is small.

CuZn (β brass): The equiatomic CuZn alloy is metallurgically similar to the AgCd alloy just discussed.[15] The major difference is that the Cu $3d$ states lie closer to E_F than the $4d$ states of Ag, so that s-d hybridization gives rise to an appreciable unoccupied d character above E_F, usually estimated as 0.3 d holes. The role of these states in the relaxation (screening) process must be examined.

If δR is initially ignored in the calculation of charge transfer, a value of $\delta z = 0.02 \pm 0.04$, somewhat smaller than most other estimates, is obtained using data from Ref. 18. Mott[19] obtained ±0.075 from the ordering energy, Moruzzi *et al.*[20] −0.08 to −0.14, and Cragg and Fletcher[21] −0.086 from theoretical analyses. (Comparison with theoretical calculations is subject to the criticism that theory measures the charge within a particular volume, while the CEBE shift measures a $1/r$ weighted charge distribution.[22])

The magnitude of the relaxation correction can be estimated using the relaxation energy for Cu from Ref. 11 of 3 eV per $3d$ electron and an independent estimate of charge transfer. Using the value of −0.075 for the charge transfer leads to the conclusion that all 0.3 empty d states become filled in the alloy, and implies that there is significant charge flow from s into d states. The valence-band spectra of Cu and β brass shown in Ref. 18 are in accord with this result, showing the Cu d band 0.25 eV narrower and 0.5 eV deeper in the alloy. The same behavior is seen in the band-structure calculations of Ref. 11 which show dramatic d band narrowing in the alloy.

AuZn: This intermetallic compound differs from those discussed so far in the larger electronegativity difference between the constituents, 0.2, 0.3, and 0.8 for AgCd, CuZn, and AuZn, respectively. The upper edge of the d band of gold is 2 eV below E_F, just like that of Cu, and the number of d holes is estimated to be 0.4.[23] The change in the d band on alloying with Zn is much greater than that of Cu. The d-band centroid of AuZn lies 1.1 eV deeper, and the bandwidth is reduced by 1.7 eV; see Fig. 1. (The Au $5d$ states in AuZn retain a clear indication of d-d interaction, just like the $3d$ states of Cu in CuZn.) These observations suggest substantial filling of the empty d states of metallic gold on formation of the AuZn alloy. This filling requires explicit consideration of the relaxation term, whose magnitude per d electron is not known. In the absence of the relaxation correction the estimated charge transfer is only −0.05 ± 0.03. If we take the relaxation energy per d electron to be the same as in Cu and assume that the d states are filled in AuZn we obtain a relaxation energy of 1.2 eV and a charge transfer of −0.20 ± 0.05. This calculation neglects the expansion of the negative gold ion, which reduces the Coulomb integral. In the present formulation this effect is largely nullified by the corresponding contraction of the Zn ion. Compared to the atomic radii deduced from the lattice constants

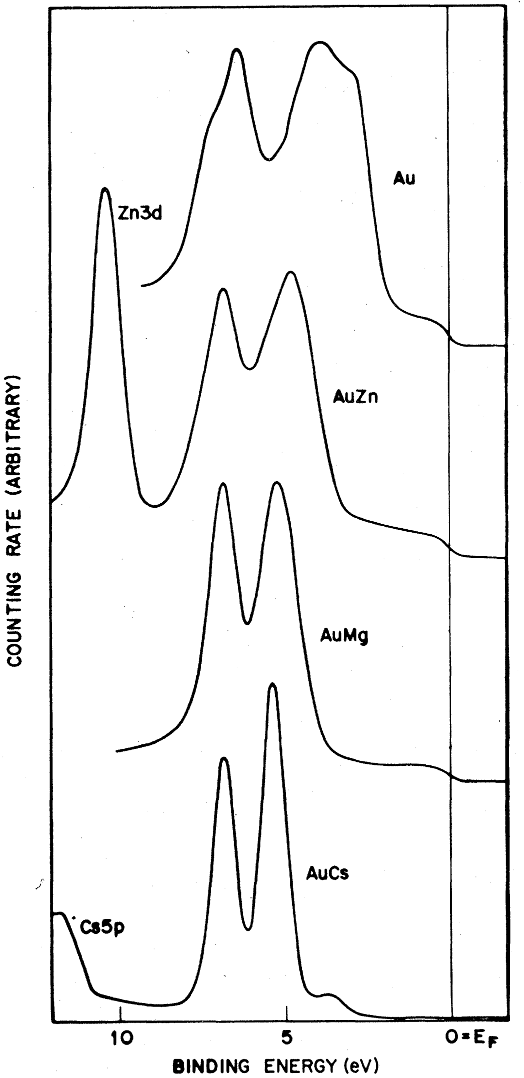

FIG. 1. XPS valence-band spectra of Au, and some CsCl-structure Au intermetallic compounds. Obtained with monochromatized Al $K\alpha$ radiation.

of the pure metals there remains a net 6% expansion in AuZn. This has the effect of decreasing the denominator in Eq. (2) by about 20%. With this change the charge transfer calculated as above becomes -0.25 ± 0.05.

AuMg: The electronegativity difference here is 1.2, and the valence-band structure resembles that of ionic insulating AuCs more closely than that of metallic Au, Fig. 1. In the absence of the relaxation correction the charge transfer is -0.12 ± 0.04, significantly larger than the corresponding estimate for AuZn. With the assumption that the *d* band is completely filled, allowing for a net 8% expansion, and using the value of the relaxation energy obtained above, the charge transfer to Au is -0.4 ± 0.1.

Support for the assumptions regarding the screening correction made in the above analyses comes from the observation that the alloy Fermi levels *calculated* using the same parameters generally fall between those of the constituents, as one would expect; see Table I. Without the relaxation term unrealistically small work functions are obtained for the alloys.

AuCs: Data[24] on this semiconducting CsCl structure compound are included to show the nature of the Au $5d$ band in the ionic limit. It seems appropriate to use that terminology because the $5d$ spectrum is reduced to a spin-orbit doublet with the free-ion spin-orbit splitting of 1.5 eV. Charge transfer in this material has been variously estimated to lie in the range from -0.5 to -0.8.[24–26] Band-structure calculations[27] show a filled Au $5d$ band well below E_F and a Au $6s$ valence band. The band gap is 2.6 eV. Small admixture of Cs $5d$ and $6s$ states into the valence band reduces the Au $6s$ character below the nominal $5d^{10}6s^2$ configuration.

IV. RESULTS: MOSSBAUER MEASUREMENTS

Mössbauer data are shown in Fig. 2, along with least-squares fits using Lorentzian line shapes. Numerical values of isomer shifts obtained from the fits are shown in Table II, and plotted in Fig. 3. For all the samples except the AuZn, the observed linewidths correspond to the natural width (1.85 mm/sec), slightly increased by thickness broadening. The AuZn sample showed a significantly broader line, probably due to lattice disorder. In AuAg and AuCu, in which both ordered and disordered states exist, the order-disorder transition has been shown to produce only small changes in the isomer shift.[28] Thus, we consider the AuZn data valid regardless of the possibility of structural defects.

The Mössbauer isomer shift has been extensively studied in gold, and several good reviews discuss research on metallic[29,30] and nonmetallic[29,31] systems. The isomer shift is a parameter unique to Mössbauer spectroscopy, and arises from the interaction of the electronic density at the nucleus with the change in nuclear charge radius between ground and excited states. Isomer shift measurements have the advantage that since the nuclear charge distribution is only weakly coupled ($\sim 10^{-6}$ eV) to the conduction electrons, γ-ray absorption does not result in significant excitation of the electrons. Thus, the electron density observed corresponds to that of the unperturbed electronic state. A disadvantage of isomer shift measurements is that only the total electron density at the nucleus is measured, and it is necessary to sort out contributions arising from different shells to make a physically useful interpretation of the data.

In metallic and insulating gold materials, the sys-

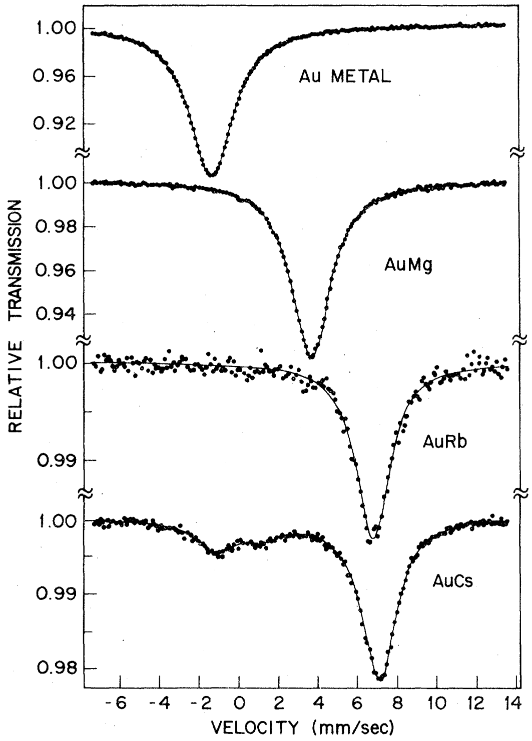

FIG. 2. Examples of Mössbauer spectra obtained in these measurements. The weak lines at ~−1 and ~+1 mm/sec in the AuCs spectrum arise from a small amount of residual metallic gold and an unidentified Au-rich Au-Cs intermetallic, respectively.

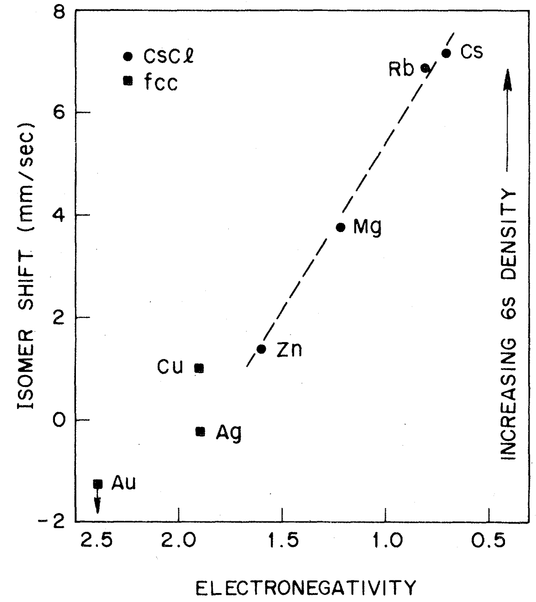

FIG. 3. Isomer shifts of the Au*X* intermetallics measured here, plotted against Pauling electronegativity values of *X*. The AuCu and AuAg values have been taken from Ref. 24, and are plotted for reference only. The arrow leading from the gold metal point is a correction to approximate the isomer shift of a fictitious bcc gold. The AuAg and AuCu points could be adjusted in the same way. The dashed line has been drawn to show the trend through the data on the bcc materials.

tematics are by now well understood, both in terms of phenomenological theory and first-principles wave-function calculations. The principal source of electron density changes is the 6*s*-electron wave function. Surprisingly, gold metal has as low an electron density as any material; even the relatively ionic gold compounds (such as AuCl, isomer shift of −0.14 mm/sec vs Au) have about the same electron density as metallic Au. This is generally explained by the strong covalency of gold compounds, so that 6*s*-electron transfer to the ligands is not complete.

TABLE II. Linewidths and isomer shifts from ^{197}Au Mössbauer spectra of materials discussed in text. Stated errors are 1σ values from least-squares fits. Isomer shift values have been corrected (Ref. 29) ($\leq$0.01 mm/sec) for the dispersion term.

Material	FWHM (mm/sec)	Isomer shift[a] (mm/sec)	6*s* electron transfer to Au (8 mm/sec = $6s^1$)
AuZn	3.40	1.37 ± 0.01	0.3
AuMg	2.40	3.736 ± 0.002	0.6
AuRb	2.06	6.81 ± 0.01	1.0
AuCs	2.06	7.09 ± 0.06	1.0
Au	2.70	−1.261 ± 0.003	. . .

[a] Relative to a Au:Pt source.

Calibrations of the gold isomer shift have been performed in three ways: from the pressure dependence of the isomer shift in gold metal, from isomer shifts of gold as a dilute solute in Cu and other metals (supported by pseudopotential calculations), and from isomer shift systematics of mono-, tri-, and pentavalent gold compounds. Each of these experiments leads to an isomer shift calibration of +8 mm/sec per 6*s* electron transferred to the gold. Shifts from other terms are relatively small: removal of 5*d* electrons, which serves to draw in the 6*s* and 5*s* wave functions and increase their density at the nucleus, provides only a small change. From isomer shift differences among Au(I), Au(III), and Au(V) compounds, it can be estimated that removal of a 5*d* electron leads to an increased density corresponding to only ~+1 mm/sec. Changes in 6*p* population would be expected to have even less effect on the isomer shift.

The isomer shift results are summarized in Table

II. They show that the gold in AuCs has one full 6s electron more than gold metal does. This result is in agreement with the description of this compound as "ionic". In this isostructural series the isomer shift is proportional to the AuX electronegativity difference.

V. DISCUSSION

A large fraction of the charge transfer obtained from the CEBE shifts derives from the relaxation term. There is a simple basis for this result which is peculiar to the noble metals. Consider a pure metal with some empty d states and an alloy in which the d states are filled. In the metal the energy of a core hole state is reduced by final-state relaxation involving the empty d states. In the alloy the initial-state energy is reduced by the extra d charge, but the final-state relaxation is less effective. The two cases tend to result in the same binding energy (relative to vacuum), because the initial-state effect of charge transfer is effectively cancelled by the difference in final-state relaxation energy. If the relaxation term is ignored CEBE shifts yield fictitiously small values for charge transfer. Combined with large s-electron transfer from isomer shift measurements, one is then led to postulate compensating d- to s-charge flow. In the present materials the valence-band spectra clearly show the d band approaching the atomiclike d^{10} state with increasing charge transfer to the gold, requiring gain rather than loss of d electrons.

A consistent picture of charge flow may be obtained, starting with the configuration of metallic gold from APW calculations[23] which yield $5d^{9.6}6s^{0.9}6p^{0.5}$. Note first of all that the gain of an entire s electron in AuCs, according to the isomer shift data, then implies a $6s^{1.9}$ configuration. This is considerably greater than other estimates and suggests that the isomer shift calibration constant may be too small by as much as 25%. The other s-electron charge transfers are then similarly overestimated. However, without invoking such a recalibration both XPS and Mössbauer-effect data for AuZn are satisfied within their uncertainties by a gold configuration $5d^{10-x}6s^{1.2}6p^{0.05+x}$. For AuMg a configuration $5d^{10}6s^{1.45}$ is indicated.

Large electron transfer values like those obtained here violate the Pauling electroneutrality principle. It had been proposed many years ago that back transfer of d electrons from the gold could allow both the electroneutrality principle and the Mössbauer isomer shift results to be satisfied.[32] The combination of XPS and isomer shift results has allowed additional information to be obtained. Recent analyses[3,4] have concluded, for compounds similar to those that we have studied here, that electron transfer out of d states is important in reducing the net flow of electrons to gold. However, the XPS valence-band spectra themselves are unequivocal—they show that as the ligand electronegativity decreases, the gold 5d electrons are more tightly bound and behave more like electrons in a filled shell. If the net charge on the gold in AuCs were to be small (i.e., ~0.1 electron), this would require essentially one 5d shell hole to cancel the gain of one 6s electron indicated by the Mössbauer isomer shift. In a case in which the XPS spectrum shows d states with atomic character lying 7 eV below the Fermi level this is clearly an untenable proposal. Thus we conclude that net electron transfer to the gold must be fairly large, in accord with the results shown in Table I.

The anomalous behavior of AuMg, i.e., its high melting point, appears in the present context to be the results of the nearly ionic character of the material. It has a large electron transfer to Au, and a d-band structure more like ionic AuCs than metallic AuZn.

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[*] Permanent address: Institut für Festkörperforschung, KFA, 5170 Jülich, W. Germany.

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