

Valence electronic structure of AuZn and AuMg alloys derived from a new way of analyzing Auger-parameter shifts

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A new model is presented that makes it possible to determine the degree of electron transfer in alloys from measurements of the Auger parameter. This approach is superior to the use of core-ionization-energy shifts in conjunction with a potential model. The Auger parameter does not depend on any reference level, whereas ionization energies measured with respect to the Fermi level must be corrected to the vacuum level before they can be used in the potential model. Furthermore, the new model does not require inclusion of contributions from Madelung, surface-dipole, or other bulk contributions, which must be considered in the potential model. This new technique is applied to the alloys AuZn and AuMg to show that approximately $0.1e$ is transferred to the gold in the first case and about $0.2e$ in the second. The analysis shows that there is a small increase in the gold $5d$ population through the series Au, AuZn, AuMg. The results are combined with data on Mössbauer isomer shifts and theoretical band-structure calculations for Au to give a description of the valence electronic configuration in these alloys. The substantial transfer of electrons to the gold $6s$ orbital, inferred from the Mössbauer results, is partially offset by back transfer of $6p$ electrons from gold to the partner atom. This conclusion is supported by band-structure calculations for AuCs.

I. INTRODUCTION

A fundamental chemical question is "what electronic changes take place when atoms combine to form molecules or solids?" Where there are large electronegativity differences between the components, electron transfer will take place. Where electronegativity differences are small, there will be electron sharing rather than electron transfer. In either case, there may be changes in the electronic configuration from that of a free atom. It is of interest to determine quantitatively the extent to which each of these occurs.

Alloys provide useful systems to investigate this question since it is possible to vary the electronegativity difference between the components over a reasonably wide range while keeping the structure essentially unchanged. There have been a number of studies¹⁻⁵ in which Mössbauer shifts and core-ionization-energy shifts are used to provide insight into the degree of charge transfer between the different kinds of atoms in binary alloys. In each of these, the analysis of the core-ionization-energy shifts has involved a potential model and is plagued by a host of difficulties. These will be considered in more detail in the Discussion section; here we note only one problem. That is, we cannot analyze ionization-energy shifts to give the ground-state charge distribution without making a correction for final-state charge rearrangement (screening of the core hole, or relaxation). Previous studies have either presented reasons for ignoring this correction or estimated the correction on the basis of some plausible ideas.

An experimental measurement of the relaxation-energy shifts can be obtained from the Auger-parameter shifts (the sum of ionization- and Auger-energy shifts). In the course of analyzing such data we have found that the

Auger-parameter shifts themselves can be used to determine the ground-state charge distribution in alloys. The method for doing this is free from most of the problems that affect the potential model. We present here a discussion of this new relaxation model and its application to finding the charge distribution in AuZn and AuMg from values of the Auger parameter that we have measured.

The alloys AuZn, AuMg, and AuCs provide an interesting series for such investigations, with the electronegativity difference between gold and the other element ranging from high for AuCs to relatively low in AuZn. Charge transfer in these alloys has been studied by Wertheim, Cohen, Creelius, West, and Wernick,⁵ who measured both core-ionization-energy shifts and Mössbauer isomer shifts. From their analysis they concluded that in each alloy there is significant electron transfer from the electropositive metal to gold, ranging from $0.25e$ for AuZn to $0.4e$ for AuMg and $0.7e$ for AuCs. They also concluded that there is no back transfer of d electrons from the gold to the other element of the alloy, which might have partially neutralized the large transfer of electrons to the $6s$ orbitals of gold.

In order to provide a clearer picture of the electronic configuration in these alloys, we have measured appropriate Auger kinetic energies in Au, Zn, Mg, AuZn, and AuMg and have remeasured the core-ionization energies. As noted above, our original interest had been to use the Auger parameter as a measure of the relaxation energy so that we could analyze the data using the potential model. Instead, we have developed a new model that uses the Auger parameter directly to give the ground-state charge distribution. We have combined the results of this analysis with the Mössbauer data given by Wertheim *et al.*⁵ and theoretical calculations of the electronic configuration in gold metal^{6,7} to give a picture of the configu-

ration in AuZn and AuMg. The results obtained for the degree of charge transfer and for the gold electronic configuration are intermediate between calculated results for Au, where there is no electron transfer, and for AuCs,⁸ where gold is alloyed with an element more electropositive than either zinc or magnesium.

II. EXPERIMENTAL

The AuMg and AuZn alloys were prepared for us by Metal Crystals (Cambridge). We verified their composition by measuring the intensities of appropriate photoelectron lines, using relative photoelectric cross sections given by Scofield,⁹ and estimating average escape depths in the alloys from the data given by Penn.¹⁰ The compositions obtained in this way were Au₅₅Mg₄₅ and Au₄₆Zn₅₄. The composition of the AuZn alloy was also measured by x-ray fluorescence, and found to be Au₄₇Zn₅₃, in good agreement with that found by electron spectroscopy.

X-ray diffraction analysis of powder samples showed that the alloys have the expected CsCl structure. For the AuMg alloy the patterns were sharp with little diffuse background. A sample of AuZn taken by filing powder from a larger piece showed somewhat diffuse lines and considerable diffuse background. A second sample cut from a rolled sheet of AuZn showed a much sharper pattern with less diffuse background. It is possible that the original sample has some substitutional disorder that is removed by rolling.

The electron spectra were measured in a modified AEI ES200 spectrometer. For the core lines, monochromated Al $K\alpha$ x rays were used. Each series of measurements involved determination of the position of the Fermi edge as well as the position of the lines of interest. Thus the core-ionization energies could be determined relative to the Fermi energy without knowledge of the exact x-ray energy, which depends on the particular adjustment of the monochromator. In order to bring the Auger kinetic energies to the same reference point, it is necessary to add the work function of the spectrometer to the measured Auger kinetic energies. This was determined by measuring the position of known core lines with unmonochromated Al $K\alpha$ x rays, whose average energy is accurately known to be 1486.55 eV.¹¹ Then K_A^F , the Auger kinetic energy relative to the Fermi energy, is given by the expression

$$K_A^F = 1486.55 + K_A - K_C - I_C^F, \quad (1)$$

where K_A and K_C are positions of the Auger and core lines measured on the instrument scale, and I_C^F is the core-ionization energy (relative to the Fermi level) as determined in the measurements with monochromated x rays. For the magnesium KLL and zinc $L_{23}M_{45}M_{45}$ Auger measurements all lines were excited with x rays from an aluminum anode. For gold we have used the $M_{45}N_{67}N_{67}$ Auger transitions, which create final states in the core of the atom. The spectra show sharp multiplet structure (Fig. 1), and it is possible to measure the shifts in Auger energy with suitable accuracy. These transitions were excited with a silver anode, and the sample was

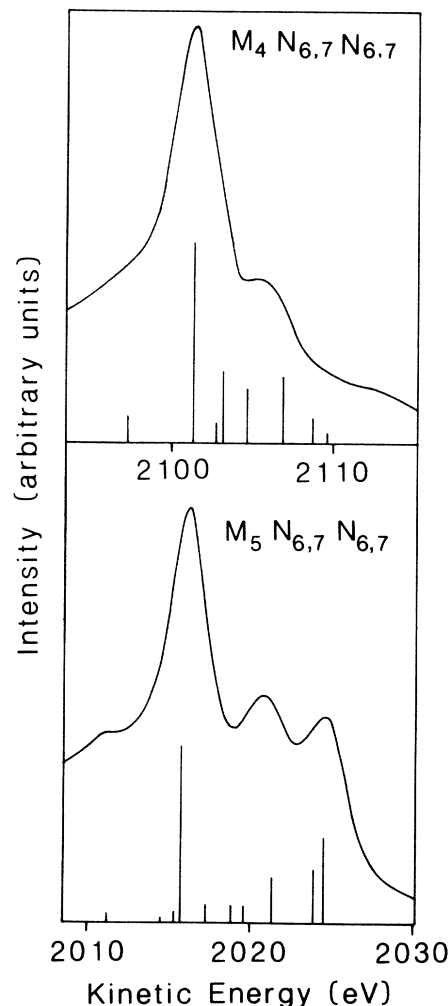


FIG. 1. The $M_{4,5}N_{6,7}N_{6,7}$ Auger spectra of Au. The energy scale is referred to the Fermi energy. The bars represent the calculated position and intensity of components of the $4f^{12}$ multiplet structure (Ref. 13).

biased to +800 V to bring the Auger electrons within the kinetic energy range of the analyzer. Gold $4f$ lines were then excited using aluminum x rays with the sample under the same bias. The bias cancels out of Eq. (1), and therefore does not have to be known accurately.

The samples were cleaned of surface contaminants by scraping with a tungsten carbide blade. Zn, Au, and AuZn could be cleaned to the point that no oxygen peak was visible in the photoelectron spectrum and remained in this state for many hours. It was, however, impossible to remove all traces of oxygen from the AuMg, and significant oxygen contamination built up within about an hour. All measurements reported here for AuMg involved short periods of measurement interspersed with cleaning to remove the oxide. The shape and position of the magnesium lines changed over a period of hours without cleaning, but the gold lines were unaffected by oxygen build up. The preparation of clean surfaces by scraping should yield

TABLE I. Experimental core-ionization energies and Auger kinetic energies. All are relative to the Fermi energy. All are given in eV. Experimental accuracy ± 0.05 eV.

	Au	Zn	Mg	AuZn	AuMg
Core-ionization energies					
Au $4f_{7/2}$	84.04			84.68	84.78
Au $4f_{5/2}$	87.71			88.34	88.46
Zn $2p_{3/2}$		1021.60		1021.58	
Mg $1s$			1303.2 ^a		1303.54
Auger kinetic energies					
Au $M_5N_{67}N_{67}^b$	2015.61			2015.16	2015.04
Au $M_4N_{67}N_{67}^b$	2101.07			2100.67	2100.44
Zn $L_3M_{45}M_{45}^1G_4$		992.22		991.92	
Mg $KL_{23}L_{23}^1D_2$			1185.8 ^a		1184.81

^aReference 27.

^bMeasurement of the most intense component which has mainly 1I_6 character.

a surface representative of the bulk composition: This view is supported for AuZn by the agreement found between the x-ray photoemission spectroscopy (XPS) and x ray fluorescence determinations of the alloy composition. Surface enrichment of one constituent is known to occur in such alloy systems, and this can be exacerbated by preferential etching if the Ar-ion-bombardment cleaning technique is used. However, it is possible that mechanical scraping changes the local order particularly in the easily deformed AuZn alloy. Since the x-ray diffraction experiments on AuZn showed a difference between the "as-received" sample and a rolled sample, we attempted to see if there was any difference in the photoelectron spectra of these samples. In one experiment we mounted on the same holder samples of rolled AuZn and as-received AuZn. By adjustment of the position of the sample holder we could measure the spectrum from either sample alone. These measurements showed that the gold $4f$ ionization energy for the rolled sample is about 0.1 eV higher than for the as-received sample. This difference grew smaller as the sample was scraped. No difference was apparent in the zinc ionization energies for the two samples. The valence-band XPS spectra of Au, AuZn, and AuMg were found to be identical to those reported by Wertheim *et al.*⁵

In our analysis we shall assume that the measured changes in the kinetic energies of the Auger transitions reflect environmental changes experienced in the core of the atoms and not in the valence level structure. This is known to be the case for the Mg KLL transitions which have been extensively studied.¹² The assumption should be valid for the Au $M_{4,5}N_{6,7}N_{6,7}$ transitions which create final hole states in the $4f$ shell. The observed spectral shape of these transitions agrees with atomic structure calculations¹³ (Fig. 1) and the spectra observed from Au, AuZn, and AuMg had identical profiles. The assumption might be questioned for the Zn $L_{2,3}M_{4,5}M_{4,5}$ transitions which involve the Zn d levels. However, we feel it should be reasonably valid since the final states have large binding energies, ~ 30 eV; they are known to be localized on a single site¹² and the transitions had the same spectral shape in Zn and AuZn.

The experimental results are given in Table I. In Table II we list the shifts in ionization energy, ΔI , and Auger kinetic energy, ΔK , for each component of the alloys (relative to the corresponding quantities in the pure metals). Except for the value of zinc in AuZn, the ionization-energy shifts agree within 0.1 eV of those reported by Wertheim *et al.*⁵ For the one exception the disagreement is 0.17 eV. We have repeated this measurement several times, with good reproducibility.

Also shown in Table II are the shifts in Auger parameter, given by the expression

$$\Delta\alpha = \Delta I + \Delta K \quad (2)$$

TABLE II. Ionization- and Auger-energy shifts between alloy and pure metal. Auger-parameter shifts derived from the experimental data (in eV). (Shifts are all for the given element in the alloy relative to the same element in the pure metal.)

	AuZn		AuMg	
ΔI (Au)	0.64		0.74	
ΔI (Zn-Mg)		-0.02		0.34
ΔK (Au)	-0.42		-0.60	
ΔK (Zn-Mg)		-0.30		-0.99
$\Delta\alpha$ (Au)	0.22		0.14	
$\Delta\alpha$ (Zn-Mg)		-0.32		-0.65

This quantity is approximately twice the relaxation energy. We see that these are small, in keeping with the assumption made by Watson and co-workers,¹⁻⁴ but not in agreement with the relaxation corrections made by Wertheim *et al.*⁵ They estimated the difference, $\Delta R(\text{Au}) - \Delta R(\text{Zn/Mg})$, to be -1.2 eV, compared with $+0.3$ to 0.4 from our experimental measurements. The conclusions they have reached using the potential model are, therefore, subject to some doubt.

III. MODEL FOR THE AUGER PARAMETER

At its simplest, the potential model can be expressed in the following form for a binary compound:

$$\Delta V = \Delta q(k - M), \quad (3)$$

where ΔV is the average potential felt by a core electron in the atom of interest relative to that for the same species in a reference material. The factor Δq is the relative valence charge on the atom of interest and k is the change in potential when a valence electron is removed. The Madelung term M represents the effect of the charge distribution in the extra-atomic environment on the potential at the core.

Application of the potential model to determining ionicity in crystals is beset by problems. First, because of a near cancellation of k and M in typical systems, ΔV is remarkably insensitive to the ionicity, Δq .¹⁴ Moreover, the relative uncertainty in the difference, $k - M$, may be quite large, even though the absolute uncertainty in k itself is small. Second, one must correct the measured ionization-energy shifts for final-state relaxation and must add the work function (usually either unknown or poorly known) to ionization energies measured relative to the Fermi level in order to reference them to the vacuum level. Uncertainties in the correction are often larger than the measured shifts. Finally, in solids, ΔV depends not only on the terms indicated in Eq. (3), but also in changes in the surface dipole between the substances of interest and, possibly, on differential compression of the valence electrons in the different solids.^{15,16} These quantities are poorly known.

Whereas the ionization energy depends directly on the potential at the core, the Auger parameter depends on the change in the potential at the core when an inner-shell electron is removed. For a metal, this change is entirely due to changes taking place at the core-ionized atom—shrinkage of the valence orbitals and transfer of a screening charge from the surroundings. There is no polarization of the surrounding metal and no change in average surface dipole from the creation of a single core-ionized atom. Because the surroundings do not contribute to the Auger parameter, we will not have the problems that result in the potential model from the near cancellation of k and M . From an experimental view, the Auger parameter depends on the difference between two kinetic energies from the same sample and does not depend on the work function or reference level. Thus, both theoretically and experimentally, the Auger parameter provides significant advantages over the ionization energy as a probe of charge distribution, provided that we have a suitable model for relating the measured quantities to the desired ones. We now present such a model, first in summary to show the basic principles involved and then in detail to show its application to the problem at hand.

From the work of Thomas¹⁷ it can be shown that the Auger-parameter shift $\Delta\alpha$ can be written as

$$\Delta\alpha = \Delta[q(dk/dN) + (k - 2dk/dN)(dq/dN) + dU/dN], \quad (4)$$

where q and k have the same significance as in Eq. (3) and U is the potential due to the surroundings. The derivatives are with respect to the occupation number N of the core orbitals. It has been assumed here that both k and q vary linearly with N . The first term represents the relaxation contribution from shrinkage of the occupied valence orbitals when the atom is core ionized, and the second represents the contribution from transfer of screening charge from the surroundings to the core-ionized atom. The third gives the effect of polarization of the surroundings by the core hole; in conductors, this is zero and will be ignored.

In metals, dq/dN is one, since exactly one screening electron is attracted from the conduction band. Then, in a comparison of two metals, $\Delta(dq/dN)$ is zero and we have

$$\Delta\alpha = \Delta q(dk/dN). \quad (5)$$

As will be seen below, dk/dN can be determined from a set of Dirac-Fock calculations, and is found to range from -1.5 to -3.5 V for the elements of interest to us. Thus Δq can be readily determined from the Auger-parameter shift.

In a more general case, the substance of interest may differ from the reference compound in the occupancy of more than one valence orbital. Then Eq. (4) becomes

$$\Delta\alpha = \Delta \sum_i [q_i(dk_i/dN) + (k_i - 2dk_i/dN)(dq_i/dN)]. \quad (6)$$

Since Δq_i and dq_i/dN both are zero for fully occupied orbitals, the sum may involve only a few orbitals, namely, the partially occupied valence orbitals. We consider the specific situation for a ground-state valence configuration $d^{10-x} s^y$ and a core-ionized, screened configuration $d^{10-u} s^{y-x+u+1}$. Then we can show that

$$\begin{aligned} \Delta\alpha = & \Delta x(k_d - k_s - dk_d/dN + dk_s/dN) \\ & - \Delta u(k_d - k_s - 2dk_d/dN + 2dk_s/dN) \\ & + \Delta q(dk_s/dN), \end{aligned} \quad (7)$$

where Δx represents the difference in d charge between the two compounds and Δu the difference in d screening following core ionization. The usual situation of interest involves nd and $(n+1)s$, where n is the principal quantum number. We make the plausible assumption that the screening electron will fill any empty nd orbitals before filling the empty $(n+1)s$ orbitals. Then either $u = x - 1$ and $\Delta u = \Delta x$ or $\Delta u = 0$. For gold we will be concerned with the latter case and Eq. (7) becomes

$$\Delta\alpha = \Delta x(k_d - k_s - dk_d/dN + dk_s/dN) + \Delta q(dk_s/dN). \quad (8)$$

In the limit of filled d orbitals, $\Delta x = 0$ and Eq. (8) becomes identical to Eq. (5). For the AuMg and AuZn alloys, we can apply Eq. (5) to the Auger-parameter shifts for magnesium and zinc to obtain the total charge transfer, Δq , in each alloy. Combining this with the Auger-parameter shift for gold and using Eq. (8), we obtain Δx , the change in charge for the gold $5d$ orbitals. The Mössbauer isomer shifts give the change in $6s$ population on gold. Combining all of these results gives a

complete picture of the valence electronic structure of gold in these alloys.

IV. THE PARAMETERS

In order to use Eqs. (5) and (8) to analyze the Auger-parameter shifts, we must have values for k and its derivatives with respect to core occupancy. In the potential model, k is the change in potential at the core when a valence electron is removed. More formally,

$$k = -\partial V / \partial n, \quad (9)$$

where n is the number of valence electrons.

Frequently, k has been equated to $\langle 1/r \rangle$, the expectation value for the reciprocal valence radius, or to F , the Coulomb integral between a valence electron and the core electron. As has been pointed out several times,^{2,18,19} these approximations ignore the role of passive electrons when a valence electron is removed. This effect can be seen in a straightforward manner. The potential felt by a core electron because of n valence electrons is $-nF$. When one valence electron is removed, the potential changes by $-\partial V / \partial n$, which is given by

$$-\partial V / \partial n = F + n(\partial F / \partial n). \quad (10)$$

Since the valence shell expands when valence electrons are added and contracts when they are removed, $\partial F / \partial n$ is negative and k should be smaller than would be calculated from F alone.

Another choice has been to equate k to the difference in core-ionization energies for a free neutral atom and a free atom that has lost one valence electron.²⁰ These energies will, however, differ not only because of changes in the initial-state potential due to removal of the valence electron, but also because of changes in relaxation energy because of the change in the number of electrons. We may readily show that this free-atom-free-ion difference, ΔI , is given by the expression

$$\Delta I = k - (dk/dN)/2, \quad (11)$$

where the first term represents the initial-state effect and the second term the relaxation. Since dk/dN is negative, ΔI is larger than k .

The appropriate choice for k , at least for free atoms, is the change in orbital energy when a valence electron is removed, since the orbital energies depend on the initial-state potential and not on final-state relaxation. As indicated above, this will be smaller than either F or ΔI . The orbital energies can be readily evaluated for the relevant species by Dirac-Fock calculations.²¹ Values of k calculated in this way for the atoms of interest here are given in Table III, where they are compared with values of ΔI (also obtained from Dirac-Fock calculations as the difference in energy for the four appropriate atomic-ionic species²²) and F (from Aoyagi *et al.*²³). We see that $k < \Delta I < F$, as discussed above.

While the foregoing discussion is satisfactory when applied to free atoms, it must be modified for atoms in molecules or solids. Because of overlap of the wave functions of adjacent atoms, the charge density near an atom in a molecule or solid will be higher than the charge density at an equivalent point near a free atom. Moreover, we will be concerned not with the total charge centered on a particular atom (which may actually be closer to some adjacent atom than to the one of interest), but with the total charge associated with that volume of the solid or molecule that can be assigned to the atom of interest. In a homonuclear crystal this volume is the Wigner-Seitz cell. Watson and co-workers^{1-4,24} have dealt with this problem by truncating the valence wave functions at the surface of the Wigner-Seitz sphere and then renormalizing the remaining wave function within this sphere. Using these wave functions and an appropriate version of Eq. (10), they have calculated k for $6s$ and $5d$ electrons of gold interacting with the $4f$ electrons. Their values are given in Table III in the column headed k' . To obtain values for magnesium and zinc we have performed a similar truncation and renormalization procedure, starting with known Hartree-Fock wave functions.²⁵ We then estimate k' from the expression

$$k' = k \langle 1/r \rangle_{\text{truncated}} / \langle 1/r \rangle_{\text{free atom}}, \quad (12)$$

where $\langle 1/r \rangle$ is the expectation value for the reciprocal valence radius. These values are also listed in Table III. We see that the values of k' are considerably larger than

TABLE III. Theoretical estimates of potential parameters (in eV).

	k^a	ΔI^b	F^c	k'^d	dk/dN^e	dk/dN^f	dk/dN^g
Mg(1s, 3s) ^h	8.84	10.25	11.12	11.39	-2.82	-4.19	-3.49
Zn(2p, 4s) ^h	9.31	10.54	12.79	12.11	-2.46	-2.36	-2.52
Au(4f, 6s) ^h	8.38	9.19	11.24	12.9 ⁱ	-1.62	-1.55	-1.64
Au(4f, 5d) ^h	12.21	13.16	20.34	16.2 ⁱ	-1.90	-2.01	-2.09

^aDifference in Koopmans's energy between neutral atom and valence-ionized atom.

^bDifference in core-ionization energy between neutral atom and valence-ionized atom.

^cCoulomb integral between valence electron and core electron.

^dBased on renormalization to unit charge within the Wigner-Seitz radius. See text.

^eCalculated from Eq. (11) and values of ΔI and k given in this table.

^fDifference between k for neutral atom and k for core-ionized atom.

^gFrom equivalent-cores approximation. See text.

^hCore electron; valence electron.

ⁱReference 2.

the free-atom values, k , and are approximately the same as the values of F . Because of a near cancellation of two opposing effects, the free-atom values of F appear to be reasonable approximations to appropriate values of k for use in solids.

Watson's method of renormalization²⁴ probably overestimates k' , since it raises the electron density by a constant factor throughout the entire atom. However, the increased electron density comes from contributions from neighboring atoms, and the greatest increase should be near the surface of the Wigner-Seitz cell. A simple model illustrates this question. We take a cluster of one atom surrounded by 12 nearest neighbors in cubic-close-packed symmetry. The valence electron density for a single atom is taken to vary as $r^2 \exp(-\alpha r)$, where α is chosen so that half the density lies outside the Wigner-Seitz radius, R_{WS} . The total density at any point is the sum of the contributions from all 13 atoms. By considering only the density within the Wigner-Seitz cell, we can obtain an appropriate value for $\langle 1/r \rangle$. In units of R_{WS}^{-1} , the value of $\langle 1/r \rangle$ so obtained is 1.45, compared with 1.17 from the free-atom density and 1.60 from Watson's procedure of truncating the free-atom density at R_{WS} and renormalizing. A fourth estimate of 1.30 comes from truncating the free-atom density at R_{WS} and then adding in the missing charge at this radius. We see that the value given by Watson's prescription is higher than that obtained by the other approaches and is, in this case, higher than would be obtained from distributing an electron uniformly through the volume of the Wigner-Seitz sphere (1.5). We conclude, therefore, that the free-atom value k and the renormalized-atom value k' bracket the correct value.

We turn now to a choice of values for the derivatives dk/dN . These may be obtained for free atoms by three methods. First, we may use Eq. (11) and the values of ΔI and k from Table III. The resulting values are given in the fifth column of numbers in Table III. Second, we assume that k varies linearly with N . Then dk/dN is the difference between k for the neutral atom and k for the core-ionized species, the k values being obtained from Dirac-Fock calculations. Values obtained by this method are shown in the sixth column. To provide a third estimate we use the equivalent-cores approximation and obtain k from Dirac-Fock calculations in which the core-ionized magnesium, zinc, and gold atoms are replaced respectively by aluminum, gallium, and mercury ions having the same valence configuration. Then we equate k for the core-ionized atom of atomic number Z to k for atom $Z+1$ with a missing valence electron. The results are given in the last column of Table III. These three ways of estimating dk/dN produce similar results for zinc and gold. The values of -4.19 and -2.82 for magnesium (as well as the value of ΔI for magnesium) are of questionable reliability since these results all involve a Dirac-Fock calculation for a magnesium ion with two open s shells, $1s$ and $3s$. To get this calculation to converge it was necessary to omit off-diagonal Lagrange multipliers.²¹ This procedure can have a large effect²⁶ on the results of the calculation for configurations with inner-shell holes. Consequently, we use the equivalent-cores value of dk/dN for magnesium in the analysis that follows rather

than the values based on the other methods.

The values of dk/dN listed in Table III are appropriate for free atoms. Presumably we should use higher values in the solid. As an approximation, we assume that dk'/dN is equal to $(dk/dN)k'/k$, and, in keeping with our earlier discussion, treat this value as an upper limit.

Finally, we must consider the role of valence p electrons. Magnesium metal is thought²⁷ to have a valence configuration $3s3p$ rather than the free-atom configuration $3s^2$. Likewise, gold metal is calculated^{6,7} to be approximately $5d^{9.6}6s^{0.8}6p^{0.6}$ rather than $5d^{10}6s$, as in the free atom. Presumably $4p$ electrons contribute to the configuration of metallic zinc. In principle, we should consider a three-orbital version of Eq. (8) with appropriate values of k_d , k_s , and k_p . In practice, this is probably unnecessary. In the free atom, the p orbitals are more diffuse than the s orbitals with the same principal quantum number, with the result that k_p is less than k_s . In the solid, however, we are concerned with the charge in the Wigner-Seitz cell, rather than the charge associated with wave functions centered on a particular atom. In these circumstances, it is likely that k_s and k_p are nearly equal, and we assume this to be the case. With this assumption, no modification to Eq. (8) is necessary.

V. DISCUSSION

Before considering a quantitative analysis, we note from Table II that $\Delta\alpha$ (alloy relative to pure metal) is negative for zinc and magnesium and positive for gold in both alloys. Since dk/dN is negative, these experimental results, taken with Eq. (5), tell us immediately that there is electron transfer from zinc and magnesium to gold in the alloy. This is the expected result, given the high electronegativity of gold.

Now using the actual values of $\Delta\alpha$ and dk/dN for zinc and magnesium, we calculate the charge transfer to be between 0.10 and 0.13 for zinc and between 0.15 and 0.19 for magnesium. In each case the higher value is obtained using dk/dN for free atoms and the lower from using dk'/dN for a renormalized charge density, calculated as described above. These charges are in keeping with the relative electronegativities of the two metals. They are somewhat less than half the values obtained by Wertheim *et al.*,⁵ using the potential model and assumed corrections for relaxation energies.

With these values of Δq and the measured values of $\Delta\alpha$ for gold, we can use Eq. (8) to give the amount of charge transfer to the $5d$ orbital of gold. The values of Δx (alloy-pure metal) are between 0 and -0.01 for AuZn and between -0.03 and -0.07 for AuMg. Although these are small, they are in the direction suggested by Wertheim *et al.*⁵ They noted that the $5d$ orbitals become more bound as the ionicity of the alloy increases and, therefore, that the occupancy of these orbitals should increase as we go through the series Au, AuZn, AuMg, AuCs.

The Mössbauer isomer-shift measurements⁵ on these alloys give directly the difference in $6s$ charge between gold in the alloy and in the pure metal. These differences are $-0.3e$ for AuZn and $-0.6e$ for AuMg, with more $6s$ electrons in the alloy than in the metal in each case.

TABLE IV. Electronic configurations for gold and the alloys.

	5d	6s	6p	q (gold)	Remarks
Au	9.6	0.8	0.6	0	a
AuZn	9.6	1.1 ^b	0.4	-0.1	c
AuMg	9.7	1.4 ^b	0.1	-0.2	c
AuCs	9.8	1.6	0.1	-0.5	d
		1.8 ^b			

^aTheoretical calculations (Refs. 6 and 7).

^bBased on Mössbauer shifts (Ref. 5) and theoretical value of 0.8 for Au.

^c5d occupancy and total charge from electron spectroscopic data as described in the text. 6p by difference.

^dTheoretical calculations (Ref. 8).

There is an apparent contradiction between the small values of charge transfer that we have found and the large values of *s*-electron transfer implied by the Mössbauer results. The discrepancy is, however, only apparent. Theoretical calculations^{6,7} show that gold metal has approximately the configuration $5d^{9.6}6s^{0.8}6p^{0.6}$. Thus transfer of electrons to the 6s orbital can be balanced by back transfer of electrons from the 6p orbital. That this does happen is verified by theoretical calculations⁸ for AuCs, which give a configuration $5d^{9.8}6s^{1.6}6p^{0.1}$. We see that the transfer of one electron from cesium to the 5d and 6s orbitals of gold is partially compensated by the loss of half an electron from the 6p orbital. The possibility of back donation from the *p* orbital was considered by Watson *et al.*,¹ but was rejected because band-structure calculations available at that time did not support the view that there is substantial *p*-orbital occupancy in gold metal.

Combining the theoretical, Mössbauer, and electron spectroscopic results gives the configurations listed in Table IV. We note the following features. First, the 5d-orbital occupancy increases as we go down the series, as suggested by Wertheim *et al.*⁵ Second, the 6s-orbital occupancy increases as we go down, as required by the Mössbauer results. Furthermore, combining the Mössbauer data for AuCs relative to Au with the theoretical 6s occupancy for Au in the pure metal gives a 6s occupancy in AuCs that is quite consistent with the theoretical value for this alloy (1.8 compared with 1.6). Third, both experiment and theory show a decrease in 6p occupancy as the alloy becomes more ionic. Finally, we see that the overall ionicity increases, as expected, with increasing electronegativity difference between the two metals in the alloy.

In summary, we have developed a model that allows us to obtain the charge distribution in alloys from measurements of the Auger parameter and have applied this model to AuZn and AuMg. The results show small electron transfer to the gold, with a slightly higher value in AuMg than in AuZn. Combining these with Mössbauer data and theoretical values for the electronic configuration in Au gives the electronic configurations in the alloys. These are reasonable and fall between the theoretical results for Au and those for AuCs.

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