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Relative Fermi energies in copper-palladium alloys

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We report the results of measurements, by x-ray excited Auger spectroscopy, of the shifts of the Cu $L_{2,3}M_{4,5}M_{4,5}$ energy spectrum in the alloy $\mathrm{Cu}_x\mathrm{Pd}_{1-x}$ for various concentrations. Comparison with self-consistent coherent-potential-approximation calculations of $E_F^{\mathrm{Cu}}-E_F(x)$, the negative of the alloy Fermi energy relative to that of Cu, manifests a remarkable agreement in magnitude and concentration dependence. By resorting to a simple version of the quasiatomic model of excited-state electron screening, we demonstrate the physical origin of the various contributions to the Auger shift and show under what conditions the noble-metal Auger shift can be identified with the negative of the relative Fermi energy. Experimental evidence indicates that the charge transfer is very small (of the order of hundredths of electrons per atom) in a number of alloys containing noble metals. The nonlinear systematics exhibited by the data emphasizes the importance of considering a large number of alloys.

I. INTRODUCTION

Copper-palladium alloys have been the subject of numerous experimental and theoretical reports. These have included the following: determining valence-electronic-structure changes from x-ray photoemission spectroscopy (XPS);[1] investigating the applicability of screening models to XPS and x-ray excited Auger electron spectroscopy (XAES) data;[2] calculating valence-band electronic structure by means of the self-consistent coherent-potential approximation (CPA);[3] comparing experimental XPS valence-band spectra with theoretical results;[3,4] and studying theoretical and experimental XAES line shapes.[5,6] The results of these investigations[5,6] indicate that, although the theoretical local-valence-band density of states[3] (DOS) of the Cu atoms describes the experimental data well,[4] the theoretical Pd DOS (Ref. 3) fails to take into account a local lattice distortion around the Pd atoms[6] in dilute Pd alloys, which modifies the Pd DOS near the bottom of the d band and prevents satisfactory agreement with experiment.[5,6] Calculations of properties at the Fermi energy, however, are in good agreement with experiment.[3,7,8]

There is one property predicted by the self-consistent CPA calculations[3] which has not been compared with experiment: that is to say, the variation of the Fermi energy itself in Cu-Pd. Although the absolute value of the Fermi energy appears not to be measurable directly, since it is defined with respect to a bulk energy zero, the difference between the Fermi energies in two materials does not suffer this limitation. In particular, in metallic alloy A_xB_{1-x}, where x is the concentration of A, the difference $\Delta E_F^A(x)$ between the Fermi energy in the alloy [i.e., $E_F(x)$] and that in pure metal A (i.e., E_F^A) is involved in shifts of XPS binding energies and of XAES kinetic energies.[9-11] The Auger-energy shift ΔK_{ijk}^A of the ijk transition (i.e., i, j, and k are all core levels) of atom A is especially interesting in this context when A is a noble metal. In this case, we expect the Auger shift to be related to the relative Fermi energy under certain conditions, as follows.[11]

If $E(n_i^A,n_j^A,n_k^A)$ represents the total energy of the fully relaxed system, where n_c^A is the electron occupation of core level c of atom A (i.e., $c=i$, j, or k), then B_i^A, the binding energy of level i of species A, can be expressed[10] as

$$B_i^A=E(0,1,1)-E(1,1,1), \tag{1a}$$

and the Auger energy measured from the Fermi level is given by[10]

$$K_{ijk}^A=E(0,1,1)-E(1,0,0) \tag{1b}$$

$$=B_i^A-B_j^A-B_k^{A(j)}\ . \tag{1c}$$

The quantity $B_k^{A(j)}$ in Eq. (1c) is the binding energy of the k core level of A when there is a hole in the j level in both the initial and final states in Eq. (1a). The expressions in Eqs. (1) are based on the assumption that the system has relaxed fully before the core holes decay, so that we are dealing with long-lived holes.[11]

The Auger-energy shift relative to pure A can be cast, therefore, to a good approximation, in the form of a core-level binding-energy shift,[11-13]

$$\Delta K_{ijk}^A(x)=-\Delta B_k^{A(j)}(x)\ . \tag{2}$$

A common and simple, although naive, form for the binding-energy shift is the following:

$$\Delta B^A(x)\cong\Delta E_F^A(x)-U_d^A\delta n_d^A(x)-U_c^A\delta n_c^A(x)\ , \tag{3}$$

where δn_d^A and δn_c^A represent the change of A atom d- and conduction (i.e., sp-) electron counts, respectively, and the U's are Coulomb integrals we discuss later. Now, when A is a noble metal, the fully screened initial and final states involved in the Auger process correspond to full local d-DOS (i.e., of z^A+1 and z^A+2 atoms, respectively, where z^A is the atomic number of atom A). In other words, the valence electronic configurations of these ionized states are independent of that of the ground state except with respect to the charge transfer. Consequently, in using Eq. (3) to interpret Eq. (2), $\delta n_d^A=0$ and $\delta n_c^A=\delta^A$, the charge transfer to noble-metal atom A, so that

$$\Delta K^A_{ijk}(x) \cong -\Delta E^A_F(x) + U_c^A \delta^A(x) \ , \tag{4}$$

and we expect the noble-metal Auger shift to be a measure of the relative Fermi energy in systems with little charge transfer.

Further analysis of Eq. (2) requires a model of the core-hole screening. In this paper, we apply a simple form of the excited-atom version[14,15] of quasiatomic model (i.e., QAM) of excited-state screening to the Cu Auger shifts in the Cu_xPd_{1-x} system. This version of the QAM describes a large body of XPS and XAES data[11] and the simple form of it we employ here has been shown[16] to describe the systematics of core-hole screening in the 5d series.[17] A previous calculation[11] of Auger shifts in which charge-transfer and volume-change effects were neglected predicted that $\Delta K^A_{ijk}(x) \cong -\Delta E^A_F(x)$ when A is a noble metal. Here, we examine these effects and show under what conditions this prediction is valid.

The predictions of this model differ significantly from those of other theories[18,19] when the nature of the valence electron screening is different (i.e., d- as opposed to sp-electron screening) in the initial and final states of the transition under study (i.e., photoemission or Auger emission). The XPS binding-energy shifts of noble-metal atoms and the Auger-energy shifts of Pt-group metal atoms correspond to these situations.

Here we explore experimental consequences of the analogue of Eq. (4) and argue, from the data, that the Cu-Pd system has little charge transfer. Comparison of the measured Cu Auger-energy shifts with the relative Fermi energies from self-consistent CPA calculations[3] manifests a remarkable agreement in magnitude as well as dependence on x. Although the agreement in magnitude may be fortuitous because of variations from one self-consistent calculation[3] to another,[20] the agreement in the systematics of the concentration dependence appears to be significant, since the systematics correlate with those of other properties, such as electronic specific heat.[7]

In Sec. II we present the model and describe the underlying physical assumptions in order to interpret parameters which appear in the final expressions. In Sec. III we compare the experimental results with theory,[3] and in Sec. IV, we discuss conclusions.

II. A SIMPLE QUASIATOMIC MODEL

The binding energies in Eqs. (1) can be written in the following form:[10,11,15,21]

$$B_i^A = -\phi - \int_0^1 dn_i \varepsilon_i^A(n_i) \ , \tag{5a}$$

$$B_k^{A(j)} = -\phi - \int_0^1 dn_k \varepsilon_k^A(n_j=0,n_k) \ , \tag{5b}$$

where ϕ represents the work function; the integrands in Eqs. (5) are the self-consistently calculated energy eigenvalues (relative to the vacuum level) of the density-functional formalism,[22,23] and core-level occupancies that deviate from those of the ground state are explicitly shown. The important points here are that we must integrate over the core-level occupancy and that self-consistent charge densities (including those of the screening electrons[14]) are involved in Eqs. (5). It should be noted that the total energies in Eqs. (1) correspond to fully relaxed systems, as do all energies integrated in Eqs. (5).

To a good approximation, the shift in core-level eigenvalue relative to pure A is equal to that of the electrostatic potential energy evaluated at the nucleus.[14] In particular, from Eq. (5b), we derive,[11] for an A atom whose nucleus is at the origin,

$$\Delta\varepsilon_k^A(n_j=0,n_k) \cong -\int d^3r \, \Delta N(n_j=0,n_k;\mathbf{r}) r^{-1} \ , \tag{6a}$$

where N is the self-consistent charge density, and we use atomic units ($|e|=\hbar=m=1$). Within the region surrounding the ionized atom, the nuclear and core-electron shift contributions vanish and $\Delta N = -\Delta\rho$, where ρ is the self-consistent valence electron density,

$$\rho(n_j=0,n_k;\mathbf{r}) \equiv \sum_v n_v |\psi_v(n_j=0,n_k;\mathbf{r})|^2 \ . \tag{6b}$$

The quantity ψ_v in Eq. (6b) is a self-consistent valence electron solution of the Kohn-Sham[23] equations for the given core-level occupancy, and ρ includes the self-consistent screening charge of the core holes.[14] In a study of self-consistently-calculated static screening of chemisorbed atoms with core holes on jellium metals, Lang and Williams[14] showed that the screening structure resembles that of adding a valence electron (if the valence level is available) to an impurity with one more proton (i.e., z^A+1) and that the metal behaves as a structureless source of screening electrons. Because of the screening, we expect modification of the ψ_v only near the origin. Consequently, the influence of the core hole in Eq. (6a) is restricted to the vicinity of the ionized atom, and we can define a minimum volume V_I within which the screening charge completely compensates that of the core holes. We can then separate the electrostatic potential-energy difference in Eq. (6a) into an integral over V_I and one over the external volume which extends to infinity and includes the surface dipole barrier. Calling this latter contribution $\Delta\Phi_E^A$, we can write[11]

$$\Delta\varepsilon_k^A(n_j=0,n_k) \cong \int_{V_I} d^3r \, \Delta\rho(n_j=0,n_k;\mathbf{r}) r^{-1} + \Delta\Phi_E^A \ . \tag{7}$$

The approximation leading to Eq. (6a) (Ref. 14) (i.e., treating the k-core wave function as spatially localized) is not essential within V_I: we could just as well retain the core-level probability density, which results in a Slater integral in Eq. (7), without changing the arguments that follow. For simplicity we retain the form in Eq. (7), with the understanding that we may interpret the Coulomb integrals as Slater integrals in calculations.

The principal effects of the core holes are twofold: that of modifying the valence wave functions and pulling initially unoccupied states below the Fermi energy, and that of attracting screening electrons to these states.[14] These effects are interrelated. The Coulomb integrals depend directly on the core-hole occupation through the field of the additional positive charge and indirectly through the additional screening electron occupation.

All the effects of alloying on the charge density, such as charge transfer, in the external region are included in Φ_E. For spherical V_I, Φ_E equals the average over the surface of V_I of the electrostatic potential energy due to all charges external to V_I (we choose the zero of energy at infinity). For truly random alloys, this average is site independent and it seems reasonable to identify $\Delta\Phi_E^A$ with the difference of dipole barrier potential energies. When, as in the case of Pd atoms in dilute Pd alloys of CuPd, there is a local distortion of the lattice, Φ_E is site dependent and this identification is questionable.

Combining Eqs. (2), (5b), and (7) yields, for alloy A_xB_{1-x},

$$\Delta K_{ijk}^A(x) \cong \Delta\phi^A(x) - \Delta\Phi_E^A(x) + \int_0^1 dn_k[P^A(x;0,n_k) - P^A(1;0,n_k)] \ , \tag{8a}$$

$$P^A(x;n_j,n_k) \equiv \sum_v n_v(x;n_j,n_k)U_v(x;n_j,n_k) \ , \tag{8b}$$

$$U_v(x;n_j,n_k) \equiv \int_{V_I} d^3r|\psi_v(x;n_j,n_k;\mathbf{r})|^2 r^{-1} \ . \tag{8c}$$

In Eqs. (8), the core electron occupation dependence of both the valence electron occupation (i.e., screening) and the valence wave functions is explicitly displayed. Up to this point, the only approximation we have made is that the influence of the core holes is limited to the central cell. When the external electrostatic potential energy is site independent, the sum of the first two terms in Eq. (8a) is a function of the concentration alone, and, as we argue above, it is reasonable to replace $\Phi_E(x) - \phi(x)$ by $E_F(x)$ (Φ_E corresponds to a bulk zero of energy from which we can measure the orbital energy shift).

According to the quasiatomic model of excited-state screening,[14,15] the screening is atomic in nature, independent of the structure of the metal. The concentration dependence of U_v in Eq. (8c) involves possible differences in ground-state electron configuration (e.g., charge transfer) as well as possible volume-change effects.

To proceed further, it is necessary to have a model of the screening. This is provided by the equivalent core model.[15] For simplicity, we consider only d and conduction (i.e., *sp*) electrons and replace the valence electron Coulomb integrals in Eq. (8b) by effective d- and c-Coulomb integrals (i.e., U_d and U_c, respectively). The equivalent core model assumes that the screening charge, which compensates the core-hole charge completely, occupies the d states first, until all are filled, and then occupies the c states. For core-level occupations $n_j=0$ and n_k, the total valence electron count is $n_d^A(x)+n_c^A(x)+1+\nu_k$, where $\nu_k=1-n_k$ is the k-level core-hole occupation and $n_d^A(x)$ $[n_c^A(x)]$ is the ground state d- (c-) electron count. When there are unfilled d states, $n_c^A(x;n_j=0,n_k)=n_c^A(x)$ and $n_d^A(x;n_j=0,n_k) = n_d^A(x)+1+\nu_k$ (as long as $n_d^A \le 10$). Otherwise, $n_d^A(x;n_j=0,n_k)=10$ and $n_c^A(x;n_j=0,n_k)=n_d^A(x) + n_c^A(x) - 9 + \nu_k$. As a result, we have Eqs. (9),

$$\Delta K_{ijk}^A(x) \cong -\Delta E_F^A(x) + \Delta P_+^A(x) + \Delta P_-^A(x) \ , \tag{9a}$$

$$P_+^A(x) \equiv \int_0^{L^A(x)} d\nu\{[n_d^A(x)+1+\nu]U_d^A(x;\nu) + n_c^A(x)U_c^A(x;\nu)\} \ , \tag{9b}$$

$$P_-^A(x) \equiv \int_{L^A(x)}^1 d\nu\{10U_d^A(x;\nu) + [n_d^A(x)+n_c^A(x)-9+\nu] \times U_c^A(x;\nu)\} \ , \tag{9c}$$

$$U_i^A(x;\nu) \equiv U_i^A(x;n_j=0,1-\nu) \cong U_i^A(x;z^A+1+\nu) \quad (i=d \text{ or } c) \ . \tag{9d}$$

In Eq. (9d), the last expression corresponds to considering the core holes as additional fractional protons. In performing the integrals in Eqs. (9), however, it is necessary only to assume that the $U_i^A(x;\nu)$ are analytic functions of ν and can be expanded in a Taylor series. The limit on the integrals $L^A(x)$ is unity (i.e., $P_-^A=0$) when $n_d^A(x) \le 8$, zero when $n_d^A(x) \ge 9$ ($P_+^A=0$, which corresponds to noble-metal Auger shifts), and $L^A(x)=9-n_d^A(x)$ otherwise.

It is interesting to note that when the nature of the screening is different in the initial and final states, it is not permissible in this model to employ a transition-state expansion in Eqs. (1).[15] This is the situation when $8 \le n_d^A(x) \le 9$, which applies to Auger shifts of the Pt group metals. Similar considerations apply to analyses of XPS binding-energy shifts,[24] and special treatment must be given to such shifts of noble metals.

Expanding the U_i^A in Eq. (9d) in a Taylor series in ν, we have

$$U_i^A(x;\nu) \cong U_i^A(\lambda;x;\nu) \equiv \sum_{s=0}^{\lambda} u_i^A(x;s)\nu^s \quad (i=d \text{ or } c) \ , \tag{10a}$$

where s is integer. When there are unfilled d states in this model [i.e., Eq (9b)], $U_d^A(x;\nu)$ and $U_c^A(x;\nu)$ depend on ν through the core-hole charge and the d-screening electrons; when the d states are full [i.e., Eq. (9c)], the c-screening electrons enter. For noble-metal Auger shifts, the screening nature does not change, and this complication does not arise, so that, for $\lambda=2$,

$$\Delta K_{ijk}^A(x) \cong -\Delta E_F^A(x) + \delta^A(x)\Omega_c^A(2;x) + \Delta V^A(2;x) \ , \tag{10b}$$

$$V^A(\lambda;x) \equiv 10\Omega_d^A(\lambda;x) + 2\Omega_c^A(\lambda;x) + Z_c^A(\lambda;x)/2 \ , \tag{10c}$$

$$\Omega_i^A(\lambda;x) \equiv [U_i^A(\lambda;x;\tfrac{1}{2}) + (\lambda-1)u_i^A(x;2)/12] \quad (i=d \text{ or } c) \ , \tag{10d}$$

$$Z_c^A(\lambda;x) \equiv [U_c^A(\lambda;x;\tfrac{2}{3}) + (\lambda-1)u_c^A(x;2)/18] \ . \tag{10e}$$

In Eqs. (10) we could employ the equivalent core expression of the Coulomb integrals [i.e.,

$U_i^A(x;\nu) \cong U_i^A(x;z^A+1+\nu)$] to facilitate interpretation. Note that the equivalent core charges are between z^A+1 and z^A+2 because of the integral in Eqs. (9).[15] The terms involving Ω_i^A in Eqs. (10) agree with the midpoint-rule approximation (i.e., the integral set equal to the integrand at $\nu=\frac{1}{2}$),[15] whereas that involving ΔZ_c^A does not [the correction is relatively minor, $u_c^A(x;1)/6$, to order $s=1$]. This discrepancy can be traced to the appearance of quadratic and higher terms in ν in the integrals in Eqs. (9), even for order $s=1$.

Since we assume that our model accurately mimics the self-consistent formation of screening charge in response to core-hole creation, the Coulomb integrals in Eqs. (10) correspond to self-consistent valence occupations appropriate to the particular equivalent core charge. Consequently, for hole occupation η [i.e., $\eta=\frac{1}{2}$ or $\frac{2}{3}$ in Eqs. (10)], the corresponding equivalent core charge is $z^A+1+\eta$, and the valence electron configuration in the Coulomb integrals is $n_d^A=10$ and $n_c^A=\delta^A+2+\eta$ [the quantities $u_i^A(x;s)$ correspond to the configuration $\eta=0$]. Expanding to first order in δ^A, we derive our final result for noble metals, in analogy with Eq. (4),

$$\Delta K_{ijk}^A(x) \cong -\Delta E_F^A(x) + \delta^A(x) W_c^A(x) + \Delta_v^A(x) \; , \qquad (11a)$$

$$W_c^A(x) \equiv \Xi_c^A(2;x) + \frac{\partial}{\partial n_c}[\Theta^A(1;x)] \; , \qquad (11b)$$

$$\Delta_v^A(x) \equiv \Delta\Theta^A(2;x) \; . \qquad (11c)$$

The quantity $\Xi_c^A = \Omega_c^A$ [i.e., Eq. (10d)] for the configuration $\eta=\frac{1}{2}$ and $\delta^A=0$. The quantity $\Theta^A(\lambda;x) \equiv V^A(\lambda;x)$ (i.e., $\lambda=1$ or 2) from Eq.(10c) for $\delta^A=0$.

Our model follows a screening prescription reported earlier.[14,15] The derivation presented here has the advantage of clarifying the physical origin of the various terms in Eqs. (11). In particular, the definition of W_c^A in Eq. (11b) is similar to that used in other work[25] and, if we neglect the deviations from the midpoint-rule approximation noted above, is approximately equal to $(\partial/\partial n_c)[\varepsilon_k^A(n_j=0,n_k=\frac{1}{2})]$ (i.e., for the self-consistent configuration with half a hole in core level k). In addition, from its definition, the term Δ_v^A is clearly a correction produced by volume-change effects alone.

Some very simple, but important, consequences follow from the form in Eq. (11a),[11] which has been employed in analysis of AuPd valence electronic structure changes.[26] We will discuss these consequences in the context of experimental interpretation in the next section.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The alloy samples studied were prepared according to procedures reported elsewhere.[1,26] The nominal bulk compositions of the samples were determined from electron microprobe analysis (0.01 error) of the homogenized alloys.

The Cu XAES measurements were performed using Al $K\alpha$ radiation (1486.6 eV) in a McPherson ESCA-36 spectrometer at a base pressure of around 1×10^{-8} Torr. The samples were cleaned *in situ* by argon-ion bombardment and then annealed (typically for 30 min at 700 °C) to remove sputter damage.[1] The effect of surface contamination on the spectra we report was found to be negligible by monitoring the spectra at various (small) levels of surface contamination as determined by the amplitude of the residual carbon 1*s* and oxygen 2*s* peaks in the XPS spectrum.

The McPherson is an electrostatic analyzer without retarding optics. It was calibrated with respect to the Au $4f_{7/2}$ line (i.e., 84.0 eV) and yielded a Au $4f_{7/2}$ full width at half maximum (FWHM) of around 1.0 eV. Measured energies were reproducible to within ±0.1 eV, so that the shifts reported are accurate to within ±0.15 eV and the differences in shifts to within ±0.2 eV. For all compositions studied, the Cu $L_{2,3}M_{4,5}M_{4,5}$ Auger line shapes[27,28] were, within experimental error, indistinguishable from the quasiatomic spectrum of pure Cu,[29] so that the whole line shape shifted rigidly.

In Fig. 1 we present, as a function of Cu concentration, results for the shifts of the principal peak of this spectrum (i.e., the ^1G term) relative to pure Cu. Displayed in the same figure are theoretical results for $E_F^{\mathrm{Cu}}-E_F(x)$ in this alloy system.[3] The remarkable agreement exhibited reflects the prediction based on the QAM that $\Delta K_{ijk}^A(x) \cong -\Delta E_F^A(x)$ for noble metal A under certain circumstances.[11,26]

In order to better appreciate the agreement manifested in Fig. 1, we can exploit the form of Eq. (11a). For z small (i.e., ~0) in alloy C_zB_{1-z} and y small in C_yA_{1-y}, where C is a noble metal, the difference in C Auger shifts is given by Eq. (12),

$$\Delta K_{ijk}^C(z\simeq0) - \Delta K_{ijk}^C(y\simeq0) \cong E_F^A - E_F^B + \Delta^C(z\simeq0) - \Delta^C(y\simeq0) \; , \qquad (12)$$

where $\Delta^C \equiv \delta^C W_C^C + \Delta_v^C$ is the sum of the charge transfer and volume corrections for atom C in each alloy. Comparing with the noble-metal atom A shift in A_xB_{1-x} for x small,

$$\Delta K_{ijk}^A(x\simeq0) \cong E_F^A - E_F^B + \Delta^A(x\simeq0) \; , \qquad (13)$$

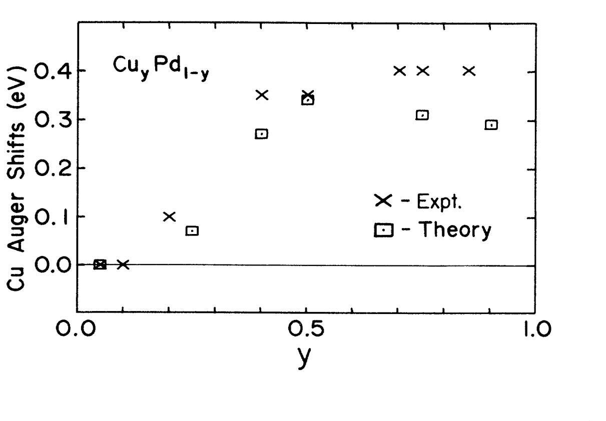

FIG. 1. Comparison of the shift of the peak energy of the ^1G term (crosses) of the Cu $L_{2,3}M_{4,5}M_{4,5}$ Auger spectrum as a function of y in Cu$_y$Pd$_{1-y}$ with theoretical values of $E_F^{\mathrm{Cu}}-E_F(y)$ (squares) from Ref. 3.

we see that the left-hand sides of Eqs. (12) and (13) would be equal if the terms in Δ^C and Δ^A could be neglected: that is, if $F(B\underline{A})\equiv -\Delta K^A_{ijk}(x\sim 0)$ in alloy A_xB_{1-x}, then the noble-metal Auger shifts would obey a transitive relation in this case, so that we would have $F(B\underline{A})=\Delta F(BA)\equiv F(B\underline{C})-F(A\underline{C})$.

Of the terms composing Δ^A (which takes its largest value in the dilute limit), we would expect Δ_v, the volume-change contribution, to be small, since $V(x)=xV_A+(1-x)V_B$ to a good approximation in the alloys we study [$V(x)$ is the alloy lattice volume and V_A is the atomic volume in metal A]. In the charge-transfer term $\delta^A W^A_C$, the coefficient is of the order of a Coulomb integral (i.e., ~ 1 Ry), so that even small charge transfers (~ 0.1 electrons/atom) would produce shifts of the order of 1 eV. In any case, we would expect no simple relationship, such as that of transitivity, to exist between the Δ^C and Δ^A terms in Eqs. (12) and (13) since they involve different noble-metal atoms in different alloys. A corollary is, therefore, that transitivity of the Auger-energy shifts in dilute alloys implies that volume and charge-transfer effects are small.

The transitivity of the Auger shifts was tested earlier.[11–13,26] In Table I, we summarize the results of these investigations. In the first two columns we present $F(B\underline{A})$,the negative of the Auger shift of the minority noble-metal component $\underline{A}$. The other columns display the difference $\Delta F(BC)$ in negative shifts of the underlined noble-metal component A between alloys $B\underline{A}$ and $C\underline{A}$. In all these examples, $F(B\underline{A})$ from the first column agrees with the corresponding value of $\Delta F(BA)$ to within ± 0.1 eV. From our previous argument, this agreement suggests that the magnitude of the volume-change and charge-transfer correction term Δ^A in these alloys is of the order of the experimental uncertainty, ± 0.15 eV. Since the volume-change and charge-transfer terms are independent, we conclude that this limit applies to them separately. Consequently, the transitivity of the Auger shifts suggests that the charge transfer to the noble-metal atoms in these alloys is of the order of hundredths of electrons per atom and that we can neglect Δ^A in Eq. (13), so that $\Delta K^A_{ijk}(x\sim 0)\cong E^A_F - E^B_F$. Furthermore, we expect Δ^A to take its largest value in the dilute limit, so that the relation $\Delta K^A_{ijk}(x)\cong -\Delta E^A_F(x)$ appears to be valid for all x for these alloys.

In particular, for $\mathrm{Cu}_x\mathrm{Pd}_{1-x}$, the agreement between the theoretical values of $-\Delta E^{\mathrm{Cu}}_F(x)$ and the measured Auger shifts in Fig. 1 independently supports the validity of this relation. It is important to note that the agreement in magnitude may be adventitious, since even self-consistent calculations do not always agree perfectly with one another.[3,20] We feel that the agreement in the systematics of the concentration variation is significant, however. For the whole concentration range there is a common theoretical[3] *d* band which approaches the Fermi energy and widens as x decreases; the Cu *d*-band high DOS decreases monotonically. The x dependence of the relative Fermi energy approximately follows that of the position of the highest theoretical density of states. For $x\leq 0.6$, the position of the common theoretical *d* band varies little with x. At higher concentrations, this band descends rapidly to preserve local charge neutrality while the Fermi energy rises until, in Cu, the *d* count is almost ten, the *d* band is full, and the DOS at the Fermi level is small. The nonlinear character of the data presented in Fig. 1 underlines the importance of considering a sufficient number of concentrations.

That the charge transfer to the noble-metal component is small in the alloys we consider is in agreement with conclusions presented in a number of studies.[3,9,30–40] The magnitude of the charge transfer adduced from our analysis (i.e., hundredths of electrons per atom), however, is considerably smaller than those reported previously (i.e., tenths of electrons per atom) for some of the same systems.[3,9,30,31,40] Since experimental analyses of XPS binding-energy shifts combined with isomer-shift measurements for Au (Refs. 9, 30, and 31) approximated the relative Fermi energy by work-function differences, it is not clear to what extent the charge-transfer magnitude difference is significant; analysis of XPS shifts in AuPd (Ref. 26) is consistent with our results. Theoretical results[3,40] employed various approximations (e.g., muffin-tin potentials) so that, again, the accuracy of the predicted charge transfer is not clear.

Our treatment here involves exploitation of the model of complete screening of the core holes,[14,15,41–43] a model which has been shown to explain a wide variety of XPS and XAES phenomena.[11] The specific form we apply is that of the excited-atom version of the QAM,[14,15,41] whose logical consequences we investigate. Even though

TABLE I. The negative of the noble-metal Auger shifts, $F(B\underline{A})$ (in eV) in alloys $B\underline{A}$, where $\underline{A}$ is the dilute noble-metal component. Columns 1 and 2 present the alloys and shifts. The other columns exhibit the differences in negative shifts, $\Delta F(BC)\equiv F(B\underline{A})-F(C\underline{A})$, of the underlined noble metal between two alloys containing the components displayed. The error in ΔF is less than ± 0.15 eV.

$B\underline{A}$	$F(B\underline{A})$	Pd-Au	ΔF(Pd-Au)	Pd-Cu	ΔF(Pd-Cu)	Pd-Ag	ΔF(Pd-Ag)
Pd$\underline{Cu}$	−0.4	$\underline{Cu}$	−0.7	$\underline{Au}$	−0.5	$\underline{Au}$	−0.7
Au$\underline{Cu}$	0.3	$\underline{Ag}$	−0.6				
Pd$\underline{Au}$	−0.7						
Cu$\underline{Au}$	−0.2						
Ag$\underline{Au}$	0.0						
Pd$\underline{Ag}$	−0.6						
Au$\underline{Ag}$	0.0						

this treatment seems to reflect the physics of screening, as in studies of the Auger parameter in the 5*d* (Refs. 16 and 17) and 4*d* (Ref. 44) metallic series, the fact that it is a model indicates that the underlying assumptions may not be totally valid. Nevertheless, the final result in Eqs. (11) is consonant with conventional treatments and is physically appealing. Moreover, the method employed here obviates the necessity of calculating the effective Coulomb integrals, the choice of which involves considerable uncertainty,[25] and, we feel, the arguments presented seem to be quite compelling. In brief, then, what does appear to be clear is that the charge transfer is very small in these alloys, even though uncertainty regarding its order of magnitude remains. It should be pointed out that differing results for the charge transfer, which may be significant,[45] have been reported[25,45] for some intermetallic compounds.

IV. CONCLUSIONS

In this paper we present arguments that, in $\mathrm{Cu}_x\mathrm{Pd}_{1-x}$, the Cu *LVV* Auger shifts measure $E_F^{\mathrm{Cu}}-E_F(x)$, the negative of the alloy Fermi energy relative to that of Cu. In order to motivate the arguments, we present in Sec. II the derivation of Auger shifts in general based upon a simple quasiatomic model. The advantage of this derivation is that it clarifies the physical origin and interpretation of the various terms which enter the final expression for noble-metal Auger shifts. In Sec. III we present experimental results and demonstrate, for a large number of alloys containing dilute noble-metal components, that the measured noble-metal Auger shifts exhibit the transitive relation required for the identification of relative Fermi energies and negative noble-metal Auger shifts to be valid. A by-product of the transitivity is that charge transfer in these alloys appears to be small (i.e., of the order of hundredths of electrons per atom). Finally, we directly compare the measured Cu *LVV* Auger shifts and theoretical values[3] of $E_F^{\mathrm{Cu}}-E_F(x)$, and show that the agreement is remarkable in both magnitude and systematics. The nonlinear behavior of the data in Fig. 1 emphasizes the importance of measuring a large enough number of concentrations (these systematics were not observed in previous work[2]).

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