

## X-ray photoemission spectroscopy of Pt-Cu: A canonical alloy

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The possibility of employing x-ray photoemission valence-band spectra in a quantitative fashion for elucidation of valence-electron structure changes induced by alloying is examined. The special, or "canonical," property of  $\text{Pt}_{1-x}\text{Cu}_x$ , that one of the components, Pt, displays no measurable core-level shift, permits extraction of such changes from core-level and valence-band data alone. A relation between the  $d$ -resonant level shifts and the centroid of the valence-band spectra is derived and comparison of the centroid and core-level shifts leads to the desired information. The analysis indicates that there is *no* charge transfer in the system and that only Cu has significant valence occupation changes upon alloying, corresponding to dehybridization. Furthermore, information regarding Fermi-energy shifts is extracted and not required as input—the results suggest that the shifts of the Fermi levels cannot be identified with those of the work functions as in other work. Model calculations indicate that dehybridization is to be expected as an "antihybridization" effect for a narrow  $d$ -band metal in a wide  $d$ -band one.

### I. INTRODUCTION

Measurements of the electronic structure changes induced by alloying two  $d$ -band metals should clarify the nature of phenomena to which the concepts and techniques associated with translationally invariant systems are not generally applicable. In x-ray photoemission spectroscopy, or electron spectroscopy for chemical analysis (ESCA), the high kinetic energy of the photoemitted electrons raises hopes of measuring the valence-band density of states (VB DOS) directly by means of the valence band spectra (vbs) without complications introduced by final-state density of states effects. The availability of both high-resolution ESCA spectrometers and the results of band-structure calculations has encouraged systematic investigations<sup>1,2</sup> of alloy valence-band properties. The extreme sensitivity of core-level energy shifts measured by ESCA to changes in chemical environment, on the other hand, has led to work examining many-body effects upon core-level asymmetries<sup>3</sup> and to studies<sup>4-9</sup> involving quantitative determinations of electronic structure changes in alloys from core-level shifts.

In general, however, such quantitative determinations<sup>4-9</sup> are not straightforward. This can, perhaps, be best appreciated by considering the general first-order expression for  $\Delta B^A(x)$ , the measured shift in binding energy of a core level of an atom of component  $A$  at composition  $x$ , with respect to the bind-

ing energy in pure  $A$

$$\Delta B^A(x) \equiv -\Delta\omega^A(x) + \Delta E_F^A(x) \quad (1a)$$

$$\Delta\omega^A(x) \equiv \sum_v W_v^A \delta n_{vA}(x) \quad (1b)$$

$$W_v^A \equiv \frac{\partial}{\partial n_{vA}} [E(n_{vA}, n_{cA}) - 1] - E(n_{vA}, n_{cA}) \quad (1c)$$

$$\Delta E_F^A(x) \equiv E_F(x) - E_F^A; \quad \delta n_{vA}(x) \equiv n_{vA}(x) - n_{vA} \quad (1d)$$

where the quantity  $E$  is the total energy of the system,  $E_F(x)$  and  $E_F^A$  are the bulk Fermi energies in the alloy and in pure  $A$ , respectively,  $n_{vA}(x)$  and  $n_{vA}$  are the numbers of  $v$ -valence electrons/atom in the alloy and in metal  $A$ , respectively, and  $n_{cA}$  represents the number of  $c$ -core electrons/atom in pure  $A$ . In deriving Eqs. (1), we assume that  $E$  is an analytic function of  $n_{vA}$ .<sup>10,11</sup>

In order to derive the valence number changes,  $\delta n_{vA}$ , from the measured energy shifts through Eqs. (1), one is generally required<sup>4-7</sup> to make several approximations. First, the exact coefficients  $W$  are replaced by corresponding quantities calculated for atoms, with approximate prescriptions to account for the effects of relaxation and chemical environment.<sup>4-7,11-14</sup> In an ordering alloy in addition, there are expected to be Madelung contributions to the  $W$ , which are usually calculated only roughly.<sup>4-7</sup> Next, the Fermi energy change is not measured and is usually approximated by  $-\Delta\phi_A(x) \equiv \phi_A - \phi_A(x)$ , the

work function shift between pure  $A$  and the alloy.<sup>4-7,15</sup> Finally, the number of types of valence electron changes associated with both components usually exceeds the number of equations of the form of Eqs. (1) and requires that independent information be supplied (e.g., from Mössbauer spectroscopy<sup>4-7</sup>).

The possibility that the ESCA vbs yields the VBDOS would suggest that quantitative use of the vbs might help in electronic structure determinations. In particular, the shift of the resonant level characterizing the  $d$  band of a transition metal<sup>16</sup> is described by an equation similar to Eq. (1).<sup>17</sup> A study of the shifts of the resonant level (represented by the centroid of the vbs), therefore, might permit relaxation of some of the assumptions mentioned above. In this paper, we report<sup>8,9</sup> the results of a systematic study of the core-level shifts and vbs in the system  $Pt_{1-x}Cu_x$  over a wide range of concentration,  $x$ . One of the salient points presented here<sup>8,9</sup> is that  $Pt_{1-x}Cu_x$  is a *canonical* system in the sense that quantitative determination of the electronic structure changes (within the accuracy previously reported<sup>4-7</sup>) seems possible *without* any of the approximations mentioned above. Specifically our conclusions<sup>8,9</sup> are that: (i) a systematic study over a wide range of concentrations is necessary for characterization of the electronic changes induced by alloying; (ii) core-level and vbs centroid shifts are linearly related, lending support to identification of the vbs and VBDOS; (iii) the analysis yields, in the case of  $Pt_{1-x}Cu_x$ , not only the sign of  $\delta n_{vA}(x)$ , which is the usual *output* of such studies,<sup>4-7</sup> but also  $\Delta E_F^A(x)$ , which is normally treated as *input*; (iv) there is little charge transfer in the system and  $\delta n_{dPt}(x) \cong \delta n_{sPt}(x) \cong 0.0$ ; (v) calculations of integrated  $d$  character in Cu (Ref. 18) give  $0.0 \leq \delta n_{dCu}(x) \cong -\delta n_{sCu}(x) \leq 0.25$ , which, although rough, is as accurate as estimates derived usually<sup>4-7</sup> (i.e.,  $\pm 0.10$  electrons); (vi)  $\Delta E_F^{Pt} \cong \Delta E_F^{Cu} \cong 0$ , which demonstrates the dangers in identifying  $\Delta E_F$  with the difference in work function<sup>4-7,15,17,19</sup>; (vii) the observed decrease of Cu  $s$ - $d$  hybridization seems to result from the wide  $d$  band of Pt and is to be generally expected as an "antihybridization" effect<sup>9</sup> in systems with widely differing  $d$ -band widths, as has been observed.<sup>4-7</sup>

In short, this paper is concerned with unconventional methods for interpreting the data. Section II is devoted to discussion of the experimental results and Sec. III to interpretation. The physical explanation is only briefly described, along with the conclusion, in Sec. IV—more details are found elsewhere.<sup>20</sup> Preliminary reports of some of these results were published elsewhere.<sup>8,9</sup>

## II. EXPERIMENTAL RESULTS

The alloys samples were prepared in the form of thin foils by standard metallurgical techniques. Prior

to mounting in the spectrometer, each sample was annealed for 2 days at 900 °C in an  $H_2/N_2$  atmosphere to remove such dissolved impurities as oxygen and sulphur and then polished to a mirror finish. The ESCA measurements were performed in a McPherson ESCA-36 spectrometer with an  $Al K\alpha$  source at a base pressure  $\sim 1 \times 10^{-8}$  torr.<sup>8,21</sup> The samples were cleaned *in situ* by Ar-ion bombardment and then annealed (typically for 30 min at 700 °C) to remove sputter damage.

In order to illustrate the characteristic features of the pure components as well as the changes induced by alloying, we present, in Figs. 1(a), 1(b), and 1(c), typical spectra for  $Cu_{0.5}Pt_{0.5}$ , Cu, and Pt, respectively, over a binding energy range of 1000 eV. At the pressure we achieved, small amounts of carbon and oxygen impurities were always present, but the level of cleanliness was high, in general.

Narrow scans of core-level intensities as functions of binding energy are illustrated in Fig. 2 for a wide range of compositions. The Cu  $2p$  core spectra are shown in Fig. 2(a), while those for Pt  $4p_{3/2}$ , Pt  $4d_{3/2,5/2}$ , and Pt  $4f_{5/2,7/2}$  are given in Figs. 2(b), 2(c), and 2(d), respectively. The most striking feature of the Pt core spectra is that, except for Pt  $4f$  at  $x = 0.95$ , the peak positions change very little as functions of composition. From comparing with Fig. 1, we see that the shift in Pt  $4f$  at  $x = 0.95$  can be attributed to interference with the weak Cu  $3p$  lines, which overlap the same binding energy region.

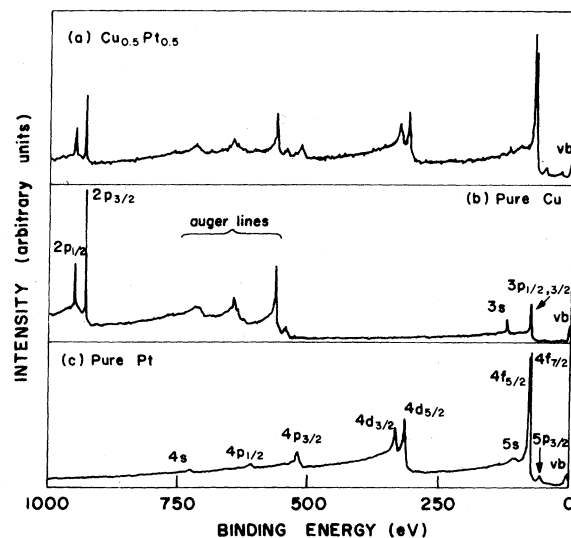


FIG. 1. X-ray photoemission spectra (XPS) over a binding energy range of 1000 eV measured from the Fermi level for (a)  $Cu_{0.5}Pt_{0.5}$ , (b) pure Cu, and (c) pure Pt. For ease of comparison, characteristic structures are identified. The spectra demonstrate the degree of cleanliness.

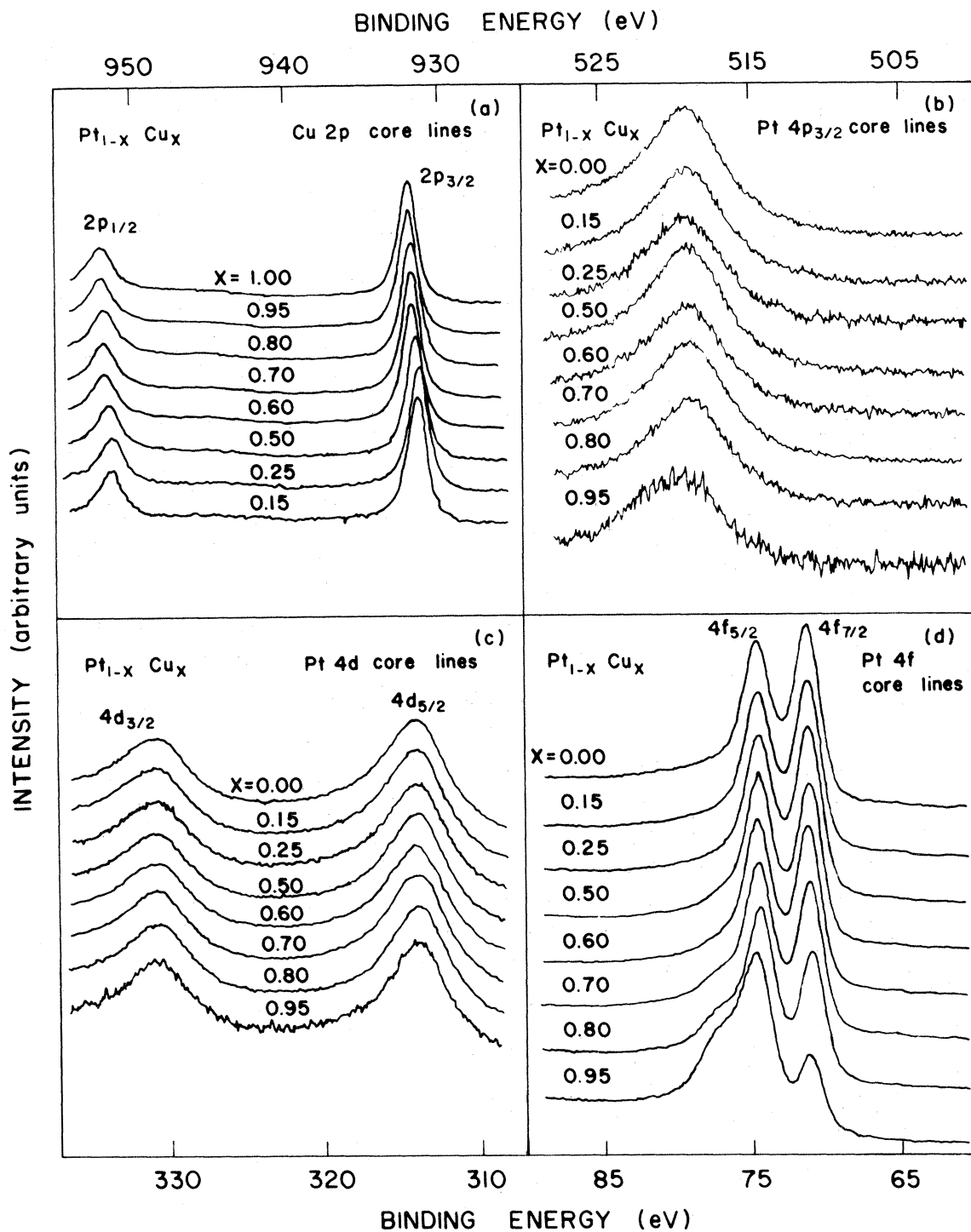


FIG. 2. Narrow XPS scans of core-level intensities for (a) Cu 2p, (b) Pt  $4p_{3/2}$ , (c) Pt 4d, and (d) Pt 4f core lines over a wide range of  $x$  in  $\text{Pt}_{1-x}\text{Cu}_x$ . The Cu shifts are evident, although the Pt position is invariant. The apparent Pt 4f shift at  $x = 0.95$  derives from interference with the weak Cu 3p line, as in Fig. 1.

Curve fitting the Pt core spectra yields  $\Delta B^{\text{Pt}}(x) = 0.0$  eV for the core levels of Figs. 2(b)–2(d) within experimental error (i.e.,  $\pm 0.10$  eV). For the Cu core spectra, however, the binding energy shifts,  $\Delta B^{\text{Cu}}(x)$ , are uniformly negative for all  $x$ , and  $\Delta B^{\text{Cu}}(x) = -0.65 \pm 0.1$  eV for all  $x \geq 0.50$  which we measure. The measured Cu and Pt binding energy shifts as functions of composition are given in Fig. 3 (in this figure,  $\Delta B^{\text{Cu}} \cong \Delta B^{\text{Pt}} \cong 0.0$  for  $x = 0.95$ ). It is, perhaps, worthwhile to point out that this is the first system reported in the literature where the core-level shifts of only one of the components changes upon alloying.

In order to yield bulk electronic structure changes, the core-level shifts must be insensitive to the condition of the surface. All of our adsorption studies show such insensitivity. Perhaps the most striking demonstration is that of Fig. 4, where we present spectra taken after three samples of widely varying composition were exposed to the atmosphere. In Fig. 4(a), the binding energy range is 1000 eV and the degree of contamination can be appreciated by comparing the spectrum for  $\text{Pt}_{0.5}\text{Cu}_{0.5}$  with the corresponding one in Fig. 1. More detailed spectra for the Cu 2*p* and Pt 4*d* core levels are illustrated in Figs. 4(b) and 4(c), respectively. Analysis of the core-level shifts yields results in concert with Fig. 3, despite the high degree of contamination of these samples.

Sputtering studies were also performed and their results also indicate surface insensitivity of the core-level shifts. Any changes can be attributed to composition changes caused by preferential sputting of the Cu.<sup>22</sup>

The VBDOS influences the core-level shifts through the valence occupation changes  $\delta n_v$  in Eqs. (1). If it is true that the ESCA vbs represents the VBDOS, then it would be interesting to use the vbs directly as independent information in addition to the  $\Delta B^A$  in order to determine  $\delta n_v$ .

In particular, the Heine-Hubbard<sup>16</sup> model of transition metal band structure characterizes the *d*-band structure of metal *A* by the  $l = 2$  resonance energy,  $E_d^A$ , which corresponds to the center of gravity of the *d* bands.<sup>23</sup> The shift of resonance energy upon alloy-

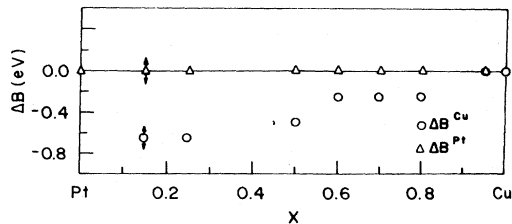


FIG. 3. Binding energy shifts as functions of  $x$  for the Cu 2*p* and Pt 4*d* lines in  $\text{Pt}_{1-x}\text{Cu}_x$ .

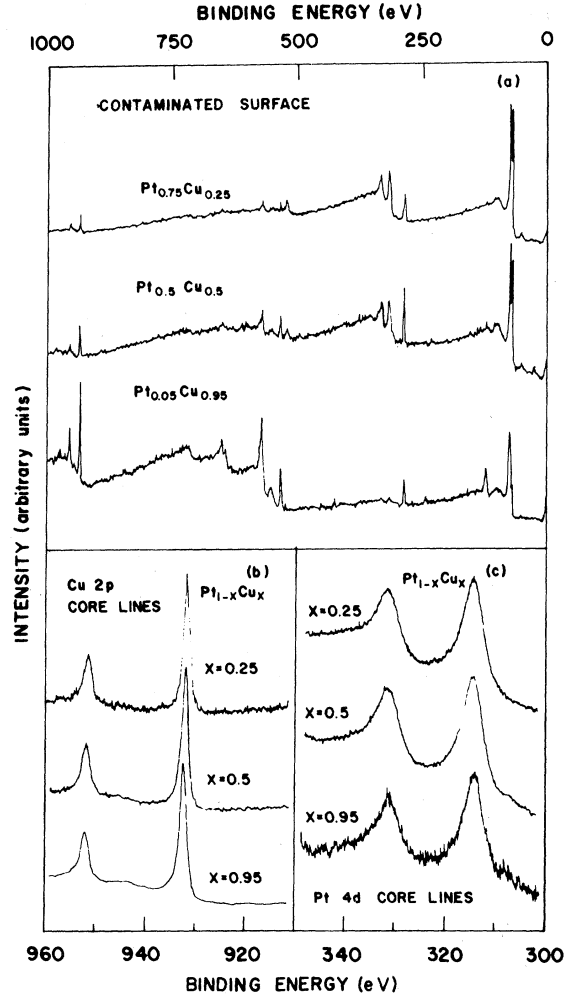


FIG. 4. XPS scans for contaminated alloy surfaces. (a) Long scans corresponding to Fig. 1(a) for  $\text{Pt}_{0.75}\text{Cu}_{0.25}$ ,  $\text{Pt}_{0.5}\text{Cu}_{0.5}$ , and  $\text{Pt}_{0.05}\text{Cu}_{0.95}$ . Degree of contamination can be appreciated by comparing with Fig. 1(a). Narrow scans for Cu 2*p* and Pt 4*d* core lines are presented in Figs. 4(b) and 4(c), respectively, for the same alloys. The peak positions are insensitive to the surface contamination, indicating the bulk nature of core-level shifts.

ing should, to first order, therefore, obey an equation similar to Eq. (1),<sup>17</sup>

$$\begin{aligned} \Delta E_d^A(x) &= \int_{-\infty}^{\infty} E dE [\rho_{dA}(x, E) - \rho_{dA}(E)] / 10 \\ &\cong U_d^A \delta n_{dA}(x) + U_s^A \delta n_{sA}(x), \end{aligned} \quad (2a)$$

$$U_v^A \cong \frac{\partial E_d^A}{\partial n_{vA}}. \quad (2b)$$

In Eq. (2a), the quantities  $\rho_{dA}(x, E)$  and  $\rho_{dA}(E)$  denote the *d*-band density of states of component *A*

in the alloy and of pure metal  $A$ , respectively.

Any measurement would sample, not  $\rho_{dA}$ , but the total VBDOS,  $\rho$ , where, in the case of  $B_{1-x}A_x$  alloys

$$\rho(x, E) \equiv \rho_d(x, E) + \rho_s(x, E) , \quad (3a)$$

$$\rho_v(x, E) = x\rho_{vA}(x, E) + (1-x)\rho_{vB}(x, E) . \quad (3b)$$

The quantity  $\rho_s$  represents the  $s$ -band density of states and subscript  $v$  symbolizes either  $s$  or  $d$ .

By analogy with Eq. (2a), it would seem that measurements should involve the shift of centroid of the total VBDOS:

$$\Delta \bar{V}(x) = \int_{-\infty}^{\infty} EdE [\rho(x, E) - \rho_w(x, E)] / 12 , \quad (4a)$$

$$\rho_w(x, E) \equiv x\rho_A(E) + (1-x)\rho_B(E) , \quad (4b)$$

$$\rho_A(E) \equiv \rho_{sA}(E) + \rho_{dA}(E) , \quad (4c)$$

where Eq. (4c) involves pure metal quantities.

In terms of the resonance energy shifts, we have

$$\Delta \bar{V}(x) = \frac{5}{6} [x\Delta E_d^A(x) + (1-x)\Delta E_d^B(x)] + \Delta V_s(x) / 6 , \quad (5a)$$

where the  $s$ -band quantity,  $\Delta V_s(x)$ , is defined by

$$\begin{aligned} \Delta V_s(x) \\ \equiv \int_{-\infty}^{\infty} EdE [\rho_s(x, E) - x\rho_{sA}(E) - (1-x)\rho_{sB}(E)] / 2 . \end{aligned} \quad (5b)$$

The vanishing of  $\Delta V_s(x)$  results from the pseudopotential<sup>24</sup> description of the conduction band states, in accord with the Heine-Hubbard model<sup>16</sup> of transition metals.

In order to apply these results to the ESCA vbs, one must consider that the experimental spectra measure the density of occupied states, and not the total VBDOS, as in Eqs. (4) and (5). In Fig. 5, we illustrate typical normalized vbs for  $Pt_{1-x}Cu_x$ , symbolized by  $g$ , as a function of binding energy for a variety of compositions. Also displayed are the corresponding weighted sums of normalized vbs of pure Pt and Cu [i.e., see Eq. (4b)] which are denoted by  $g_w$ .

Two features of the data aid in applying these results. First, only a small portion of the  $d$  bands of either Pt or Cu is unoccupied and it is concentrated in energy near the Fermi level. We have, therefore,

$$\begin{aligned} \int_{-\infty}^{\infty} EdE \rho_{dA}(E) &\equiv \int_{-\infty}^{E_F^A} EdE \rho_{dA}(E) + E_F^A \int_{E_F^A}^{\infty} dE \rho_{dA}(E) \\ &= \int_{-\infty}^{E_F^A} (E - E_F^A) dE \rho_{dA}(E) + 10E_F^A . \end{aligned} \quad (6a)$$

Applying the results in Eqs. (5)–(6a) to Eq. (4a) yields a relationship between  $\Delta V_{\text{exp}}$ , a measured valence-band quantity, and the resonance- and

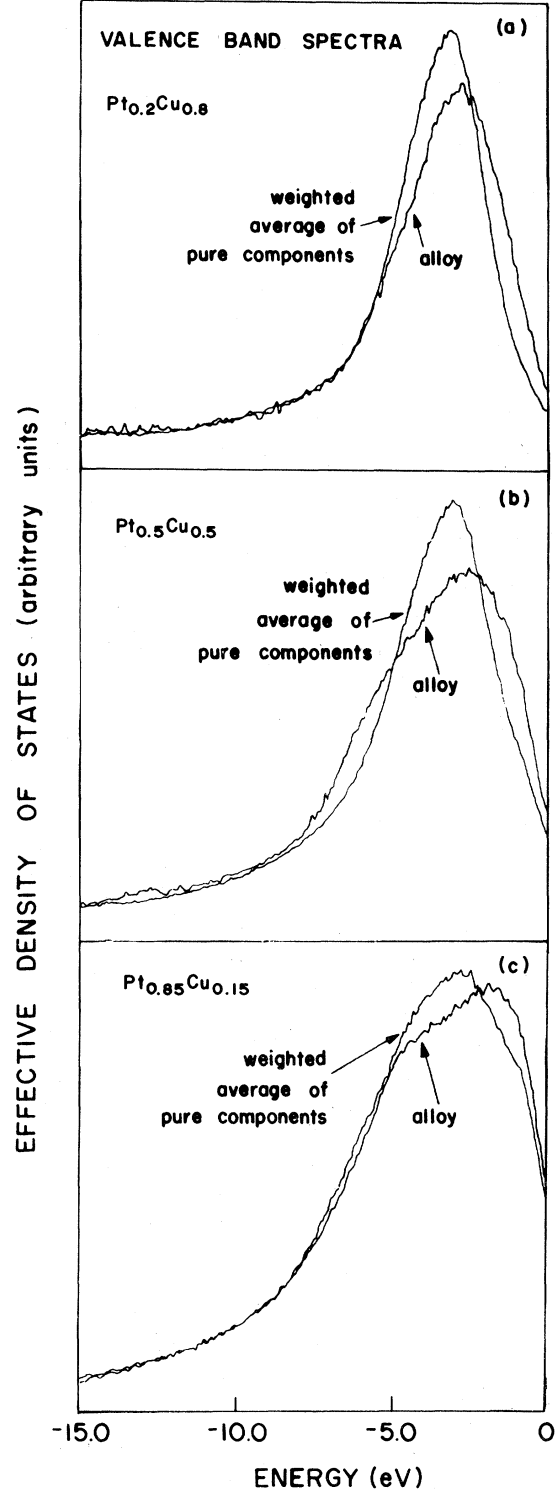


FIG. 5. Normalized valence-band spectra for three different alloys and the corresponding weighted sums of the normalized spectra of pure Pt and Cu, as in Eq. (4b).

Fermi-level shifts.

$$\begin{aligned}\Delta\bar{V}(x) &\equiv \Delta V_{\text{exp}}(x) + \frac{5}{6}\Delta E_F(x) \\ &\equiv \frac{5}{6}[x\Delta E_d^{\text{Cu}}(x) + (1-x)\Delta E_d^{\text{Pt}}(x)] ,\end{aligned}\quad (6b)$$

$$\begin{aligned}\Delta V_{\text{exp}}(x) & \\ &\equiv \int_{-\infty}^0 EdE [\rho_d(x,E) - x\rho_{d\text{Cu}}(E) - (1-x)\rho_{d\text{Pt}}(E)]/12 \\ &\equiv \int_{-\infty}^0 EdE [g(x,E) - g_w(x,E)]/12 ,\end{aligned}\quad (6c)$$

$$\Delta E_F(x) \equiv E_F(x) - xE_F^{\text{Cu}} - (1-x)E_F^{\text{Pt}} .\quad (6d)$$

In Eq. (6c), each density of state,  $\rho$  (or vbs,  $g$ ) is referred to its own Fermi level (i.e., the Fermi levels are aligned). The quantity  $\Delta E_F(x)$  is the deviation from linearity of the Fermi level, which we neglect<sup>17</sup> henceforth.

The transition from the first to the second line of Eq. (6c) is based upon the other simplifying feature of the band structure—the  $s$  densities of states of the alloy and of the constituents are closely similar and are slowly varying in the vicinity of the Fermi level. We do not expect them to contribute significantly to  $\Delta V_{\text{exp}}$ , therefore.

It would seem, at this point, that  $\Delta V_{\text{exp}}$  in Eq. (6c) is a quantity which can be determined experimentally and which can be compared with the  $\Delta B$  of Eq. (1). In practice, the influence of matrix elements causes the vbs to differ from the VB DOS. Studies of transition metals in which ESCA vbs and theoretical densities of states were compared<sup>25</sup> demonstrated appreciable modulation of the vbs by optical transition strengths for only  $5d$  metals and then for only high binding energies. Since the experimental lower limit in Eq. (6c) is finite, we use an experimental cutoff,  $E_l = -5.0$  eV, determined by the energy at which matrix elements become important in the pure metal ESCA studies.<sup>25</sup>

In order to accentuate the relation between the valence band quantities and the core-level shifts, we display, in Fig. 6, the quantity  $\Delta\bar{E}(x)$  as a function

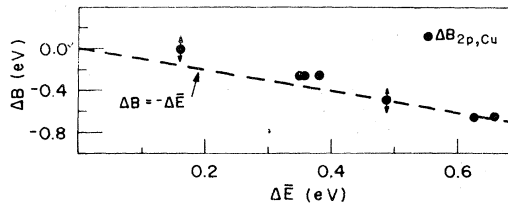


FIG. 6. Cu  $2p$  binding energy shift as a function of the shift of the valence-band quantity,  $\Delta\bar{E}$ , in Eq. (7). For reference, the line  $\Delta B = -\Delta\bar{E}$  is illustrated.

of  $\Delta B^{\text{Cu}}(x)$ , where

$$\Delta\bar{E}(x) \equiv \frac{6}{5x}\Delta V_{\text{exp}}(x) \equiv \Delta E_d^{\text{Cu}}(x) + \left(\frac{1-x}{x}\right)\Delta E_d^{\text{Pt}}(x) .\quad (7)$$

The definition in Eq. (7) serves to delineate the Cu dependence. Linearity as well as a close numerical agreement between  $\Delta\bar{E}$  and  $\Delta B$  are demonstrated clearly in Fig. 6. Perhaps even more striking is the clustering of  $\Delta\bar{E}$  corresponding to the same  $\Delta B$ . Effects of uncertainties in  $E_l$  (within  $\pm 0.5$  eV) are indicated in the size of the dots in Fig. 6. Note that this energy range includes most of the important effects of alloying.

### III. INTERPRETATION

Any interpretation of the data must explain their systematics as functions of  $x$ : that is, the valence-band centroid is a function of only the Cu core-level shift, which is uniformly negative for all  $x$ , and the Pt core-level does not shift as  $x$  is varied.

In order to shed light on our data, it is appropriate to describe what one would expect in the case of an alloy with charge transfer. Here, the charge transfer is driven by the difference in Fermi energies of the pure components<sup>17</sup> and the relation between the  $\delta_{A(B)}$ , the charge transferred to component  $A(B)$ , is determined by the charge neutrality condition,  $x\delta_A + (1-x)\delta_B = 0$ . The sharing of this charge between the  $s$ - and the  $d$ -valence states (i.e.,  $\delta_A = \delta n_{dA} + \delta n_{sA}$ ) however, is determined by the electronic structure at the constituent atom, which is governed by such Hamiltonian parameters as hopping and hybridization matrix elements<sup>17</sup> characteristic of the alloy. The presence of constituent  $B$  modifies the local density of states associated with  $A$ , but the relationship between  $\delta n_{vA}$  and  $\delta n_{vB}$  is only indirect (i.e., through the charge neutrality condition) and any correlation is expected to be weak. What this conclusion means for our data is that one expects little correlation between  $\Delta\bar{E}$  and  $\Delta B^A$  in a charge transfer system.

In order to illustrate this conclusion, we resort to results of model calculations for the  $\text{Au}_x\text{Ag}_{1-x}$  system.<sup>17</sup> In these calculations,<sup>17</sup> the pure metal Fermi energies are identified with the corresponding work functions, the pure metal electronic structures are described by  $s$ - $d$  model Hamiltonians, and the alloy is treated within the coherent potential approximation.<sup>26</sup> From the calculated<sup>17</sup> results for  $\delta n_{vA}$ , and values given<sup>17</sup> for the parameters in Eqs. (1) and (2), we derived the results for  $\Delta B$  and  $\Delta E_d$  displayed in Fig. 7(a). In this figure, we plot the resulting binding energies as functions of the respective  $d$ -resonant level

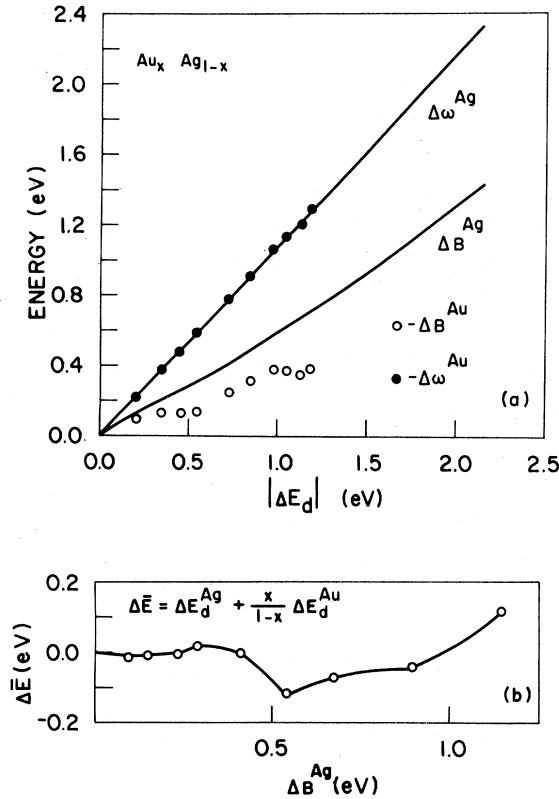


FIG. 7. (a) Results for  $\Delta\omega^A$  and  $\Delta B^A$  [see Eq. (1)] as functions of the corresponding  $|\Delta E_d|$  [see Eq. (2)] derived from model calculations for  $Au_x Ag_{1-x}$  in Ref. 17, where Ag and Au correspond to the solid lines and circles, respectively. Quantities for the same species are strongly correlated. (b)  $\Delta\bar{E}$  as a function of  $\Delta B^{Ag}$  calculated from the quantities in Fig. 7(a). The presence of  $\Delta E_d^{Au}$  removes the strong correlation in Fig. 7(b).

shift. It should be observed that the values of  $|\Delta\omega|$  [which involves only the  $\delta n$  and not the Fermi energies, as in Eq. (1b)] for both Ag and Au are almost identical linear functions of the respective  $|\Delta E_d|$  and that the slope is very close to unity, as in Fig. 6; this behavior results from the closeness of the coefficients in Eqs. (1) and (2) and is expected to hold generally. When however, we calculate the corresponding binding energies, which include the Fermi energies, the dependences deviate considerably from each other and from a line of unity slope.

The independence of the individual component resonant shifts (and the corresponding valence occupation changes) is manifested in Fig. 7(b), where we display  $\Delta\bar{E} \equiv \Delta E_d^{Ag} + [x/(1-x)]\Delta E_d^{Au}$  as a function of  $\Delta B^{Ag}$ , in analogy with Fig. 6. We interpret the absence of correlation as a consequence of the weak correlation between the shifts of the different components in a system in which charge transfer occurs.

Applying these results to the data of Fig. 6, we expect to have a linear relation between  $\Delta\bar{E}$  in Eq. (7) and  $\Delta B^{Cu}$  only if  $\Delta\bar{E} = \Delta E_d^{Cu}$ , so that  $\Delta E_d^{Pt} \leq 0.1$  eV. Such a value of  $\Delta E_d^{Pt}$  would imply from Eqs. (2) that  $\delta n_{dPt} \cong -(U_s^{Pt}/U_d^{Pt})\delta n_{sPt}$ , making  $\delta p_t \propto \delta n_{dPt}$ , so that  $\delta n_{vCu}$  would not be independent of  $\delta n_{dPt}$ . This solution would appear unphysical unless  $\delta n_{dPt} \cong \delta n_{sPt} \cong \delta p_t \cong 0.0$ . From Eqs. (1) for  $\Delta B^{Pt}$ , this implies immediately that  $E_F(x) \cong E_F^{Pt}$  for all concentrations we measure. From Figs. 2 and 3, it appears that  $\Delta B^{Cu} \cong 0.0$  for  $x = 0.95$ , implying that  $E_F^{Cu} \cong E_F^{Pt}$ , which is consistent with  $\delta p_t \cong 0.0$  (i.e., no charge transfer). The Fermi level concentration dependence deduced here is not consistent with identifying  $E_F$  with the work function.<sup>4-7,15</sup>

The Cu valence occupation changes can be derived from Eqs. (1), where  $\Delta E_F^{Cu} \cong E_F^{Pt} - E_F^{Cu} \cong 0.0$ , so that  $\delta n_{dCu} \cong -\Delta B^{Cu}/(W_d^{Cu} - W_s^{Cu}) \geq 0.0$ , that is, positive. Band structure calculations of integrated  $d$  character in Cu,<sup>18</sup> give an upper limit of 0.25 so that  $0.25 \geq \delta n_{dCu} \geq 0.0$ . The range of values imposed by these lower and upper limits is comparable to the accuracies (i.e.,  $\pm 0.10$  eV) in other studies.<sup>4-7</sup>

#### IV. DISCUSSION AND CONCLUSIONS

In this paper, we present the results of a novel approach to the derivation from ESCA data of electronic structure changes induced by alloying. We report the consequences of identifying the valence-band spectra with the density of states in a quantitative fashion. By relating the  $d$ -resonant level shift to the centroid of the  $d$  bands, we are able to express the  $d$ -resonant level shift in terms of experimentally measured quantities. From general considerations (which we illustrate in Fig. 7 with energy shift values derived from results reported in the literature<sup>17</sup>) we expect a linear correlation between the binding energy and resonant energy shifts associated with the same component, but no correlation between those associated with different components.

The special properties of the system under study,  $Pt_{1-x}Cu_x$ , permit deduction of the electronic structure changes from the ESCA core-level and valence-band data alone, with only a few, physically reasonable, assumptions (for this reason, we call the alloy system "canonical"). The Pt core level shift is zero within  $\pm 0.10$  eV for all  $x \leq 0.95$  which we measure (Fig. 3). In addition, we observe a linear correlation between the vbs centroid,  $\Delta\bar{E}$ , and  $\Delta B^{Cu}$  as manifested in Fig. 6. This implies immediately that the Pt resonant energy shift is approximately zero, lending support to our association of  $\Delta\bar{E}$  with the  $d$ -resonant shifts as in Eq. (7), since, from Fig. 7(a), one might expect  $\Delta E_d^{Pt} \cong \Delta B^{Pt} \cong 0.0$ . Furthermore, the values of the Pt shifts are physically most consistent with zero

charge transfer and a constant alloy Fermi level approximately equal to that in Pt. These shifts indicate that  $\delta n_{dPt} \cong \delta n_{sPt} \cong 0.0$ , or no change in the Pt valence occupation with alloying. From the measured trend of  $\Delta B^{Cu}$  at  $x \cong 0.95$ , we deduce further that  $E_F^{Cu} \cong E_F^{Pt}$  and that  $0.0 \leq \delta n_{dCu} \leq 0.25$ , a decrease of Cu  $s-d$  hybridization.

Although we concentrate here on methods of data analysis, it is appropriate to discuss briefly the physi-

cal origins of the results. Since the Heine-Hubbard<sup>16</sup> theory has proven so fruitful in explaining the properties of transition metals in terms of a few intuitively attractive parameters, it is desirable to explain our results on a similar basis. To this end, we posit a Hamiltonian<sup>27</sup> in the occupation number representation which describes a two component alloy  $A_x B_{1-x}$ , with a fixed total number  $N$  of atoms filling a periodic lattice and an  $x$ -independent  $s$  band,

$$H = \sum_{\vec{k}} C_{\vec{k}}^{\dagger} C_{\vec{k}} E(\vec{k}) + \sum_i C_{di}^{\dagger} C_{di} E_d^i + \sum_{\vec{k}, i} (C_{\vec{k}}^{\dagger} C_{di} \gamma_{\vec{k}i} + C_{di}^{\dagger} C_{\vec{k}} \gamma_{i\vec{k}}), \quad (8a)$$

where  $C(C^{\dagger})$  is an annihilation (creation) operator,  $i$  denotes species  $A$  or  $B$ ,  $\vec{k}$  symbolizes an  $s$ -state momentum,  $E(\vec{k})$  is the common  $s$ -band (i.e., pseudopotential) dispersion relation,<sup>24</sup> and  $\gamma_{i\vec{k}}$  is the matrix element governing hybridization of the  $d$  states with the free electron  $s$  band. In this model, we describe the  $d$  states of  $A$ , for example, only by the site-independent resonance energy  $E_d^A$ . For the case of one  $A$  atom, we have exactly<sup>20</sup>

$$\rho_A(E) = -\frac{10}{\pi} \text{Im} \left[ Z - E_d^A - S_A(E) \left( 1 + \frac{S_B(E)}{Z - E_d^B} \right)^{-1} \right]^{-1}, \quad (8b)$$

$$S_i(E) \equiv \sum_{\vec{k}} \frac{|\gamma_{i\vec{k}}|^2}{Z - E(\vec{k}) - \frac{N|\gamma_{B\vec{k}}|^2}{Z - E_d^B}}, \quad (8c)$$

$$|\gamma_{i\vec{k}}|^2 = |\gamma_i^2| \zeta_{\vec{k}}^2, \quad Z = E + i\delta, \quad (8d)$$

where  $\text{Im}$  denotes imaginary part,  $\delta \rightarrow 0^+$ , and  $\zeta_{\vec{k}}$  describes the  $k$  dependence of  $\gamma$  [i.e.;  $\zeta_{\vec{k}} \cong k^2$  for  $E(k) \cong E_d^{Cu}$  (Ref. 16)]. Details of the derivation of Eqs. (8) and a fuller discussion of the physics are given elsewhere.<sup>20</sup>

For the present, it is sufficient to note that for a narrow  $d$ -band metal  $A$ , such as Cu, in a wide  $d$ -band one  $B$ , such as Pt, we have  $|\gamma_A/\gamma_B|^2 \ll 1$  and  $\rho_A \cong 10\delta(E_d^A - E)$ : that is, a Cu impurity in Pt should look more atomic because, roughly speaking, the Cu "sees"  $d$  electrons introduced by Pt through its large hybridization matrix element. This result indicates that dehybridization is to be expected for a narrow  $d$ -band component in a wide  $d$ -band one as an "antihybridization" effect, as has been observed<sup>4,5</sup> for Ag in Ag-Au alloys. Although the inverse effect of the narrow upon the wide  $d$ -band component is more complicated, the smaller matrix element is expected to produce a much smaller effect upon the electronic structure.

From the results presented here, we conclude that

it appears possible to use the valence band ESCA spectra in a quantitative manner,<sup>9</sup> supplementing core-level data, in order to elucidate details of valence structure. From the special properties of  $Pt_{1-x}Cu_x$  over a wide range of concentrations (i.e., only one of the components, Cu, exhibits significant shifts) the ESCA data alone appear to suffice for extraction of the valence occupation changes induced by alloying. These data indicate *no* charge transfer in the system and only Cu has significant valence occupation changes, corresponding to dehybridization (as seen previously in Au alloys<sup>4,5</sup>). Furthermore, the Fermi energy shifts are extracted and *not* required as input: in the present system, it is shown that the shifts of the Fermi energies cannot be identified with those of the work functions as in other work.<sup>4-7, 15</sup>

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