

## Chemisorption on disordered binary alloys

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The problem of chemisorbing a hydrogen atom on a Cu-Ni or Au-Pt disordered binary alloy (DBA) is addressed. The DBA is modeled by a semi-infinite linear array of atomic sites each of which is randomly occupied by an atom of either component. The electronic properties of such a DBA are obtained via a Green's-function technique based on the coherent-potential (CP) approximation. The chemisorption process is described by the Anderson-Newns approach, which takes account of the intra-atomic electron interaction on the adatom. The chemisorption energy and the adatom charge transfer are then computed as a function of the alloy concentration. The calculations at the surface involve the solution of two coupled self-consistent equations, one being concerned with the CP on the surface atom and the other with the adatom occupancy. In the case of the Cu-Ni system, the effect of surface segregation is also investigated.

## I. INTRODUCTION

The electronic structure of disordered binary alloys (DBA's) has, in recent years, been the subject of much theoretical investigation<sup>1,2</sup> for which the coherent-potential approximation<sup>3</sup> (CPA) has been a primary tool. The development of techniques, such as the CPA, for the purpose of studying the bulk electronic properties of DBA's has led naturally to their use in investigations of alloy surfaces.<sup>4-8</sup> Such work is important in gaining insight into the role of alloy substrates in catalytic processes.<sup>9</sup>

Towards this end, the study of chemisorption on DBA surfaces is of particular interest. van Santen and Sachtler<sup>10,11</sup> employed a cluster model of adsorption to examine the effects on the chemisorption bond of alloying two substrate metals. The changes arising from the alloying were due primarily to modifications in the *d*-band structure. Two concepts were stressed: (a) the ensemble effect, which alters the number of substrate atoms to which the adatom bonds, and (b) the ligand effect, which changes the nature of the chemisorption bonds. From a different point of view, Moran-Lopez *et al.*<sup>8</sup> modeled the adsorbate-covered DBA surface using a continued-fraction method in conjunction with the Bethe-Peierls approximation extension of the CPA. Hence, it was possible to examine the dependence of the adatom density of states (DOS) on such factors as the concentrations of the two component metals, the adatom's position, and the strength of the adatom-substrate bonds. In addition, the adatom binding energy was found to be, in general, a monotonic

function of the alloy composition. However, they restricted themselves to adatoms of the same kind as those of the substrate, and neglected the intra-atomic Coulomb interaction on the adatom. In this way, they avoided the Hartree-Fock self-consistency problem. Furthermore, their model does not take into account the modification of the surface CP upon chemisorption, nor did they consider the effect of surface segregation.

In the present work, the CPA model of Parent *et al.*<sup>5</sup> is adopted for a DBA with a surface, which has also been utilized in the study of the electronic properties of ordered-disordered interfaces.<sup>12,13</sup> It was demonstrated that the presence of disorder produces a splitting of the localized states. Each of the two split states can be identified with a particular component atom of the DBA. The phenomenon of surface segregation<sup>14</sup> is incorporated into the model of an *A-B* alloy, in the simplest way, by confining it to the surface layer; i.e., the concentration of the *A* component is taken as the *bulk* concentration  $c_b$  in all substrate layers, except the surface one, where it is assumed to be  $c_s$ , the *surface* concentration.

In general, the surface concentration may be modified by chemisorption, but, in the case of atomic hydrogen adsorption, the modification appears to be so small as to be negligible.<sup>15</sup> The chemisorption model used here is that of Anderson-Newns (AN),<sup>16,17</sup> which within the restricted Hartree-Fock approximation involves a self-consistent calculation of the electronic charge on the adatom. Moreover, the evaluation of the CP must also be performed self-consistently, which, for the chemisorbed system, leads to a coupling of the two self-consistency conditions.

## II. SURFACE GREEN'S FUNCTION

Initially, a system consisting of an unattached hydrogen atom and a DBA, which is described by the usual tight-binding approximation, is considered. Within the CPA, the effective Hamiltonian for the prechemisorption system, illustrated in Fig. 1(a), is

$$H_0 = \epsilon_a |0\rangle\langle 0| + H_v + \sum_{i=1}^{\infty} \sigma_i(E) |i\rangle\langle i|, \quad (1)$$

where  $\epsilon_a$  is the electronic energy of the pre-adsorbed atom,  $\sigma_i(E)$  is the CP associated with the  $i$ th atomic site, and  $H_v$  is the virtual-crystal Hamiltonian for the substrate, namely,

$$H_v = \sum_{i=1}^{\infty} \alpha_i |i\rangle\langle i| - \sum_{i=1}^{\infty} J(|i\rangle\langle i+1| + |i+1\rangle\langle i|). \quad (2)$$

In (2), the virtual-crystal electronic energy at atom  $i$  is

$$\alpha_i = c_i^A \epsilon_A + c_i^B \epsilon_B, \quad (3)$$

where  $\epsilon_A$  ( $\epsilon_B$ ) is the electronic energy of an  $A$  ( $B$ ) atom and  $c_i^A$  ( $c_i^B$ ) is the concentration of the  $A$  ( $B$ ) component at the  $i$ th site of the DBA. By setting

$$c_i^A = c_i, \quad c_i^B = 1 - c_i, \quad \epsilon_A - \epsilon_B = \Delta, \quad (4)$$

Eq. (3) becomes

$$\alpha_i = c_i \Delta + \epsilon_B. \quad (5)$$

By confining surface segregation to the first (surface) layer, Eq. (5) gives

$$\alpha_i = \begin{cases} c_s \Delta + \epsilon_B, & i = 1 \\ c_b \Delta + \epsilon_B, & i > 1. \end{cases} \quad (6)$$

Moreover, the effective bond strength  $-J$  between nearest-neighbor atoms may be approximated by writing

$$J = c_b^2 J_A + 2c_b(1 - c_b) J_{AB} + (1 - c_b)^2 J_B, \quad (7)$$

$-J_A$  ( $-J_B$ ) being the bond energy between two  $A$  ( $B$ ) atoms and  $-J_{AB}$  the bond energy between  $A$  and  $B$  atoms. Hence, the effective electronic energies are

$$\sigma_s(E) = \frac{2\Delta^2 c_s (1 - c_s)}{2J_s (\xi^2 - 1)^{1/2} - 2\Delta(1 - 2c_s) + \sigma_b - 2c_s \Delta + c_b \Delta - \epsilon_B + E}. \quad (13)$$

The energies  $E_s$  of localized surface states are given by the poles of  $g_s(E)$  in (10), subject to the existence condition

$$|(c_s - c_b)\Delta + \sigma_s - \sigma_b| > |J|. \quad (14)$$

## III. ADATOM GREEN'S FUNCTION

In the chemisorbed system, represented by the model illustrated in Fig. 1(b), the adatom is attached to the sur-

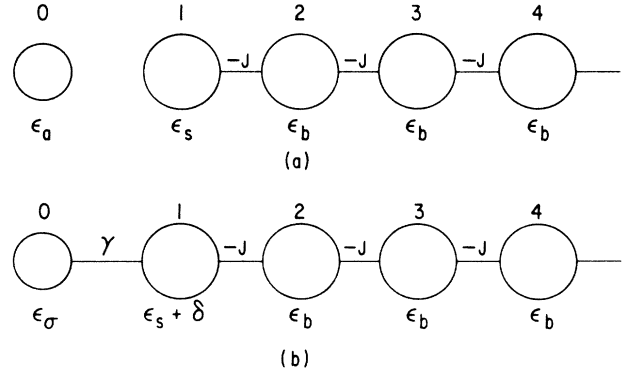


FIG. 1. One-dimensional model depicting the chemisorption process: (a) isolated hydrogen atom and DBA prior to adsorption; (b) after adsorption occurs via formation of the bond  $\gamma$ .

$$\epsilon_i = \alpha_i + \sigma_i(E) = c_i \Delta + \epsilon_B + \sigma_i(E), \quad i = s, b. \quad (8)$$

Defining the effective Green's function (GF) for the semi-infinite Hamiltonian (1) as

$$G_0(E) = (E + i0^+ - H_0)^{-1}, \quad (9)$$

the surface GF can be determined from the bulk GF (Ref. 18) via the Dyson equation, and has the explicit form

$$g_s(E) = G_0(1, 1) = [J_s (\xi^2 - 1)^{1/2} - (c_s - c_b) \Delta - \sigma_s + \sigma_b - J \xi]^{-1}, \quad (10)$$

where  $s$  is defined in (A4), and

$$\xi = (\epsilon_b - E)/2J = [c_b \Delta + \epsilon_B + \sigma_b(E) - E]/2J. \quad (11)$$

The self-consistency condition for the bulk and surface CP's is

$$\sigma_i(E) = [\Delta(1 - c_i) - \sigma_i(E)] g_i(E) [\Delta c_i + \sigma_i(E)], \quad i = s, b. \quad (12)$$

Setting  $i = s$  in (12), and performing some algebraic manipulations, gives

face atom of the substrate by a bond of energy  $\gamma$ . Within the Hartree-Fock approximation to the AN model of chemisorption,<sup>16,17</sup> the effective adatom level of spin  $\sigma$  is shifted to

$$\epsilon_\sigma = \epsilon_a + U \langle n_{a, -\sigma} \rangle, \quad (15)$$

where  $U$  is the intra-atomic Coulomb repulsion on the adatom and  $\langle n_{a, -\sigma} \rangle$  is the expected occupancy of the adatom by an electron of spin  $-\sigma$ . Here, only the non-magnetic case  $\langle n_{a\sigma} \rangle = \langle n_{a, -\sigma} \rangle$  is considered, so the subscript  $\sigma$  is suppressed, for convenience. The final effect of

chemisorption is to modify the surface CP from  $\sigma_s$  to  $\sigma_c$ . Thus, within the CPA, the effective Hamiltonian  $H_1$  for the chemisorbed system is related to the prechemisorption one (1) by

$$H_1 = H_0 + V, \quad (16)$$

the perturbation potential being given by

$$V = \epsilon' |0\rangle\langle 0| + \gamma(|0\rangle\langle 1| + |1\rangle\langle 0|) + \delta |1\rangle\langle 1|, \quad (17)$$

where

$$\epsilon' = U\langle n_a \rangle \quad (18)$$

and

$$\delta = \sigma_c - \sigma_s. \quad (19)$$

If  $G_1$  ( $G_0$ ) is the GF of the system after (before) chemisorption has occurred, then the Dyson equation corresponding to (16) is

$$G_1 = G_0 + G_0 V G_1. \quad (20)$$

Hence, the adatom and surface matrix elements are found to be

$$G_1(0,0) = \{G_0^{-1}(0,0) - \epsilon' - \gamma^2[G_0^{-1}(1,1) - \delta]\}^{-1} \quad (21)$$

and

$$G_1(1,1) = \{G_0^{-1}(1,1) - \delta - \gamma^2[G_0^{-1}(0,0) - \epsilon']\}^{-1}, \quad (22)$$

where

$$G_0(0,0) = (E - \epsilon_a)^{-1}. \quad (23)$$

The self-consistent expression for  $\sigma_c(E)$  from (12), after some rearrangement, is

$$\begin{aligned} \sigma_c = \Delta^2 c_s (1 - c_s) [J_s (\xi^2 - 1)^{1/2} - (c_s - c_b) \Delta + \sigma_b \\ - J \xi - \gamma^2 (E - \epsilon_a - U \langle n_a \rangle)^{-1} \\ - \Delta (1 - 2c_s)]^{-1}. \end{aligned} \quad (24)$$

Equation (24) indicates that the evaluation of  $\sigma_c(E)$  requires knowledge of the value of the occupation number  $\langle n_a \rangle$ , which, as will become evident in the next section, is itself dependent upon  $\sigma_c(E)$ . Thus, there is a coupling of the two self-consistency requirements.

The energy levels  $E_p$  of the localized states of the

chemisorbed system are given by the poles of  $G_1(0,0)$  in (21), which yields

$$\begin{aligned} E_p - \epsilon_a - U \langle n_a \rangle - \gamma^2 [J_s (\xi^2 - 1)^{1/2} - (c_s - c_b) \Delta - \sigma_c(E_p) \\ + \sigma_b(E_p) - J \xi]^{-1} = 0. \end{aligned} \quad (25)$$

The associated existence condition is

$$\begin{aligned} |\gamma^2 (E_p - \epsilon_a - U \langle n_a \rangle)^{-1} + (c_s - c_b) \Delta \\ + \sigma_c(E_p) - \sigma_b(E_p)| > |J|. \end{aligned} \quad (26)$$

#### IV. CHEMISORPTION PROPERTIES

When the adatom interacts with the substrate, charge transfer occurs to the adatom, resulting in the need to take account of the intra-atomic electron-electron interaction on the adatom. It is then necessary to consider the occupancy of the adatom-orbital  $|a\rangle$ , which is

$$\langle n_a \rangle = \int_{-\infty}^{\epsilon_F} \rho_a(E) dE, \quad (27)$$

where  $\epsilon_F$  is the Fermi level and

$$\rho_a(E) = -\pi^{-1} \text{Im} G_1(0,0) = -\pi^{-1} \text{Im} g_a(E) \quad (28)$$

is the adatom DOS, which, it should be noted, depends on  $\sigma_c(E)$ . When  $\epsilon_F$  lies within the  $d$  band, Eq. (27) can be written as

$$\langle n_a \rangle = -\pi^{-1} \int_{\epsilon_L}^{\epsilon_F} \text{Im} g_a(E) dE + \sum_{E_p} \text{Res} g_a(E_p), \quad (29)$$

where  $\epsilon_L$  is the lower-band-edge energy, and the summation includes all localized states below the band. In (29),

$$\text{Res} g_a(E_p) = \left[ \frac{dG_1^{-1}(0,0)}{dE} \right]^{-1} \Big|_{E=E_p}, \quad (30)$$

$G_1^{-1}(0,0)$  being given by (21). If  $\epsilon_F$  lies above the  $d$  band, then the upper limit of the integral in (29) is replaced by the upper-band-edge energy  $\epsilon_u$ , and the summation must include any localized state lying above the band, but below  $\epsilon_F$ .

Lastly, the chemisorption energy  $\Delta E$  is obtained by utilizing the Dyson equation to derive an expression for  $\Delta\rho$ , the change in the DOS caused by chemisorption. Using (20), in conjunction with (17), we obtain

$$\begin{aligned} G_1(i,j) - G_0(i,j) &= \gamma G_0(i,1) G_1(0,j) + \delta G_0(i,1) G_1(1,j) \\ &= \{\gamma^2 G_0(0,0) + \delta [1 - \epsilon' G_0(0,0)]\} G_0(i,1) G_0(1,j) \\ &\quad \times \{[1 - \epsilon' G_0(0,0)][1 - \delta G_0(1,1)] - \gamma^2 G_0(0,0) G_0(1,1)\}^{-1}, \quad i \neq 0. \end{aligned} \quad (31)$$

The change in DOS is given by

$$\Delta\rho = -\pi^{-1} \text{Im} \left[ G_1(0,0) - G_0(0,0) + \sum_{i=1}^{\infty} [G_1(i,i) - G_0(i,i)] \right], \quad (32)$$

which, as shown in the Appendix, gives

$$\Delta\rho = -\pi^{-1}\text{Im} \frac{1}{M} \left[ \epsilon' G_0^2(0,0)[1 - \delta G_0(1,1)] + \gamma^2 G_0^2(0,0)G_0(1,1) + [\gamma^2 G_0(0,0) + \delta(1 - \epsilon' G_0(0,0))] \frac{G_0^2(1,1)}{1-t^2} \right], \quad (33)$$

where

$$M = [1 - \epsilon' G_0(0,0)][1 - \delta G_0(1,1)] - \gamma^2 G_0(0,0)G_0(1,1). \quad (34)$$

The change in the one-electron energy produced by chemisorption is

$$\Delta E^{1\sigma} = E_{p1} + E_{p2} - \epsilon_a - E_z + \int_{\epsilon_L}^{\epsilon_F} (E - \epsilon_F) \Delta\rho(E) dE. \quad (35)$$

Unlike the case of chemisorption on a pure monatomic substrate, the present case gives rise to localized states in pairs at  $E_{p1}$  and  $E_{p2}$  [i.e., poles of  $G_1(0,0)$ ], if they exist at all.  $E_z$  in (35) indicates the presence of a zero of the adatom GF  $G_1(0,0)$ . When  $\epsilon_F$  lies above the upper-band edge  $\epsilon_u$ , the upper limit of integration in (35) becomes  $\epsilon_u$ . The total chemisorption energy is

$$\Delta E = 2\Delta E^{1\sigma} - U \langle n_{a\sigma} \rangle \langle n_{a,-\sigma} \rangle + \epsilon_a - \epsilon_F, \quad (36)$$

while the charge transfer from the substrate to the adatom is

$$\Delta q/e = 2 \langle n_a \rangle - 1. \quad (37)$$

## V. RESULTS AND DISCUSSION

Calculations of the chemisorption properties of Cu-Ni and Au-Pt alloys have been performed over the full range of bulk concentrations, utilizing the pure-substrate parameters found in Refs. 17 and 19.

In the case of the H/Cu-Ni system, when  $c_b = c_s$  (i.e., no surface segregation), the curve of chemisorption energy  $\Delta E$  versus bulk concentration  $c_b$  [Fig. 2(a)] displays a monotonic, almost linear, behavior. In the dilute limits,  $\Delta E$  is very close to the value for the corresponding pure system, indicating that the effect of any minority atoms

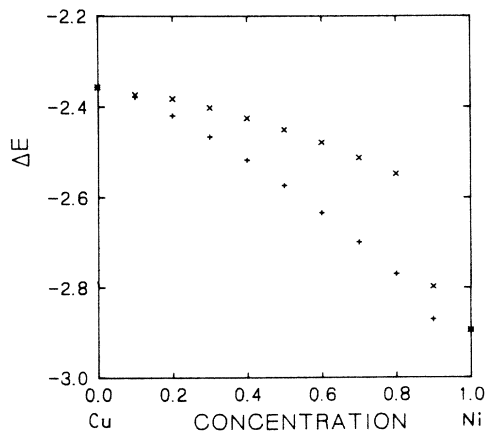


FIG. 2. Chemisorption energy  $\Delta E$  for H/Cu-Ni versus bulk Ni concentration for (a)  $c_b = c_s$  (+) and (b)  $c_b \neq c_s$  (x).

near the surface has been neutralized by the averaging process used in formulating the CPA.

On allowing  $c_s$  to differ from  $c_b$ , strikingly dissimilar results are obtained [Fig. 2(b)]. It is well established<sup>14</sup> that Cu-Ni alloys possess an enriched Cu concentration in the surface layer for all compositions (see Table I). Consequently, one would expect such alloys to exhibit a more Cu-like behavior than their nonsegregated counterparts and, indeed, this prediction is confirmed by the illustrated results. Even a small amount of Cu, added to a pure Ni substrate, produces a significant change in  $\Delta E$ , compared to the case when  $c_b = c_s$ .

Charge transfer  $\Delta q$  to the adatom for the situation  $c_b = c_s$  is shown in Fig. 3(a). The dependence of  $\Delta q$  on  $c_b$  is virtually linear, throughout the entire range of concentrations. In contrast, the presence of surface segregation [Fig. 3(b)] produces a lowering of  $\Delta q$  at all alloy concentrations (i.e., Cu segregation hinders the charge transfer process), emphasizing again the Cu-like properties of DBA's with Cu-enriched surfaces.

Graphs of the change in DOS  $\Delta\rho$  upon chemisorption versus energy  $E$  ( $< \epsilon_F$ ) are given in Figs. 4(a)–4(e) for various bulk concentrations. Starting with a pure Cu substrate ( $c_b = 0$ ), a single  $\Delta\rho$  versus  $E$  curve is obtained. On introducing Ni into the system, a satellite structure appears in the higher-energy region. Further increases in the Ni content cause the satellite to grow, and eventually merge with the main curve. Finally, the pure Ni situation is obtained when  $c_b = 1$ .

A qualitative comparison with the results of Moran-Lopez *et al.*<sup>8(b)</sup> can be made, as they also studied chemisorption energies on Cu-Ni alloys. However, they took the adatom to be Ni, rather than H, so a quantitative analysis is not possible. For  $c_s = c_b$ , the relevant curve (C1 of their Fig. 13) indicates that the binding energy is virtually a linear function of  $c_b$ , in agreement with Fig. 2(a). Although Moran-Lopez *et al.* did not specifically consider surface segregation, its effects can be approximated by the case of chemisorption onto a cluster of four

TABLE I. Surface ( $c_s$ ) versus bulk ( $c_b$ ) Ni concentration for segregated Cu-Ni alloy (adapted from Ref. 14).

	$c_s$	$c_b$
Cu	0.000	0.0
	0.001	0.1
	0.003	0.2
	0.004	0.3
	0.005	0.4
	0.010	0.5
	0.030	0.6
	0.075	0.7
	0.125	0.8
	0.300	0.9
Ni	1.000	1.0

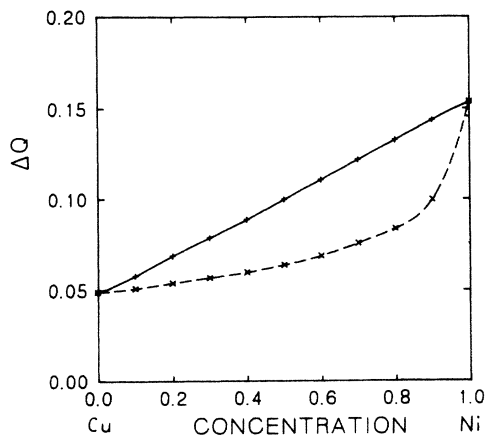


FIG. 3. Charge transfer  $\Delta q$  to the adatom for H/Cu-Ni versus bulk Ni concentration for (a)  $c_b = c_s$  (+) and (b)  $c_b \neq c_s$  (x).

Cu atoms located on the surface of the Cu-Ni alloy (curve C4). As in Fig. 2(b),  $\Delta E$  tends to be much closer to the value for a pure Cu substrate, the greatest difference from the  $c_s = c_b$  result occurring at high Ni concentration. The results of Ref. 8(b) were calculated by neglecting charge transfer from the substrate to the adatom (i.e.,  $U=0$ ), in contrast to the results presented here, indicating that the charge transfer effects do not modify the general qualitative dependence of  $\Delta E$  on  $c_b$ .

For the system of H/Au-Pt, data for surface segregation do not appear to be readily available, so only the case  $c_s = c_b$  is studied here. The chemisorption energy versus the Au concentration curve (Fig. 5) possesses a minimum at  $c_b = 0.3$ , which indicates that hydrogen is preferentially adsorbed on a Au-Pt disordered alloy at the concentration ratio of 3:7. In fact, since the absolute minimum is lower than the two end points, corresponding to Pt( $c_b = 0$ ) and

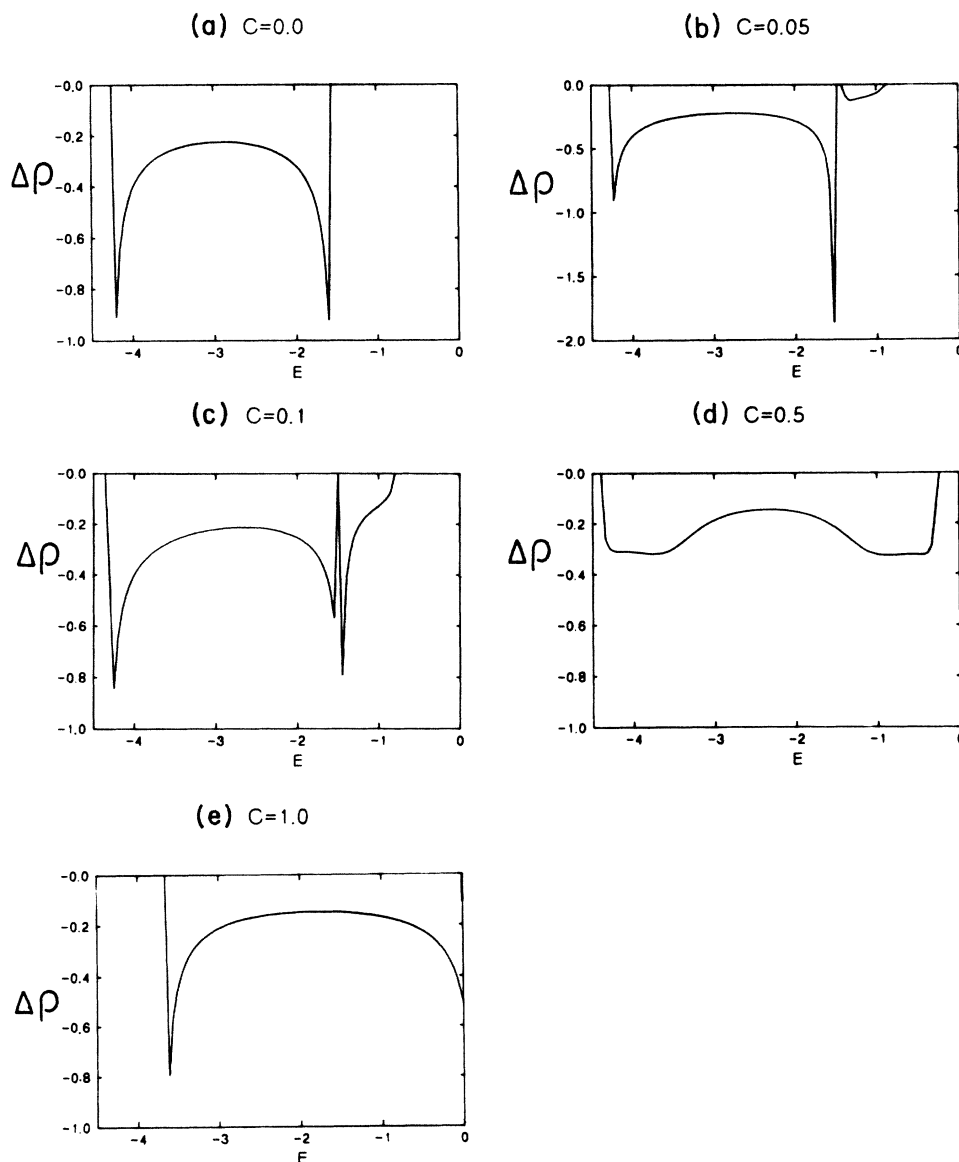


FIG. 4. Change in DOS  $\Delta\rho$  for H/Cu-Ni versus energy  $E$  for (a)  $c_b = 0.0$  (pure Cu), (b)  $c_b = 0.05$ , (c)  $c_b = 0.1$ , (d)  $c_b = 0.5$ , and (e)  $c_b = 1.0$  (pure Ni).  $c_b = c_s$ .

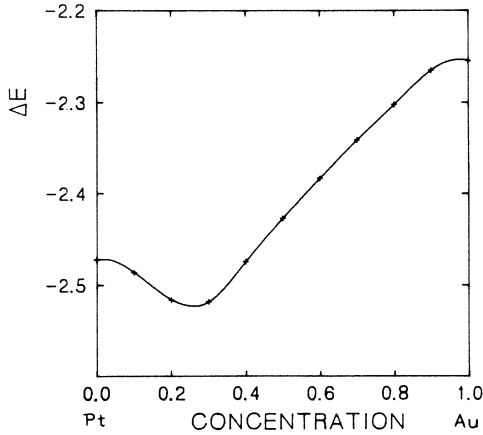


FIG. 5. Chemisorption energy  $\Delta E$  for H/Au-Pt versus bulk Au concentration for  $c_b = c_s$ .

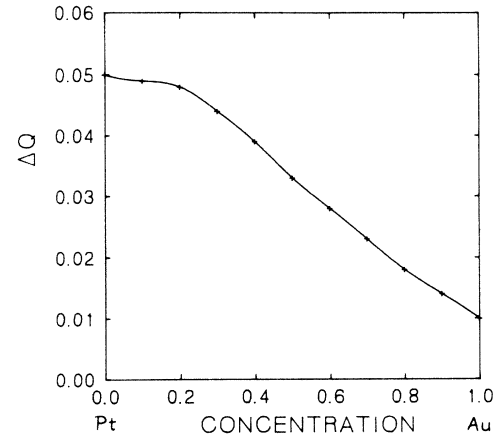


FIG. 6. Charge transfer  $\Delta q$  to the adatom for H/Au-Pt versus bulk Au concentration for  $c_b = c_s$ .

Au ( $c_b = 1$ ), the chemisorption bond is strongest there.

The charge transfer versus Au concentration graph (Fig. 6) for  $c_b = c_s$  has a slight slope at low  $c_b$  values, until it reaches the critical point ( $\sim 0.3$ ), after which the curve decreases monotonically with a marked increase in the slope.

The curves of  $\Delta\rho$  versus  $E$  ( $< \epsilon_F$ ) for the H/Au-Pt system [Figs. 7(a)–7(d)] exhibit a structure similar to that of the H/Cu-Ni situation, but without any satellite structure

arising from the presence of Pt in Au.

In summary, a theory of chemisorption on binary alloys has been presented. Model calculations on the systems of H/Cu-Ni and H/Au-Pt have been performed. In the former system, the effect of surface segregation manifests itself as an increase in the chemisorption energy as compared to the nonsegregated case, while in the latter system, the phenomenon of preferential chemisorption is predicted.

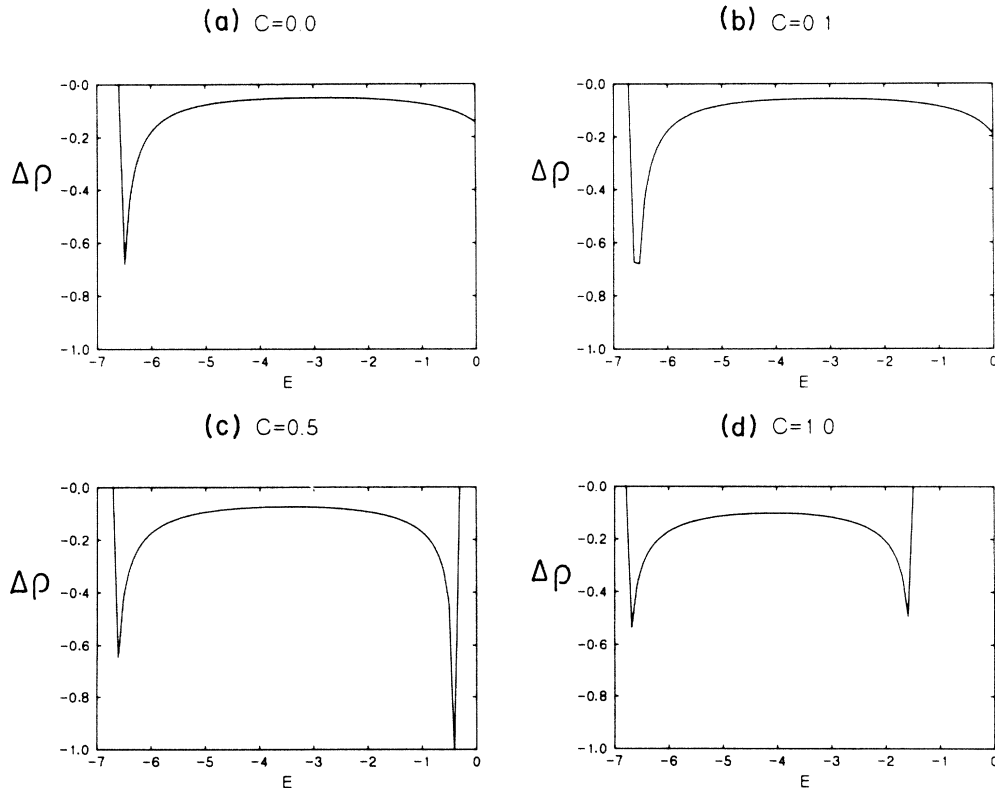


FIG. 7. Change in DOS  $\Delta\rho$  for H/Au-Pt versus energy  $E$  for (a)  $c_b = 0.0$  (pure Pt), (b)  $c_b = 0.1$ , (c)  $c_b = 0.5$ , (d)  $c_b = 1.0$  (pure Au).  $c_b = c_s$ .

## ACKNOWLEDGMENT

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## APPENDIX: EVALUATION OF EQ. (33)

Equation (33) is obtained by using (31) in (32) with  $i = j$ , which yields

$$\Delta\rho = -\pi^{-1} \text{Im} \frac{1}{M} \left[ \epsilon' G_0^2(0,0) [1 - \delta G_0(1,1)] + \gamma^2 G_0^2(0,0) G_0(1,1) + [\gamma^2 G_0(0,0) + \delta(1 - \epsilon' G_0(0,0))] \sum_{i=1}^{\infty} G_0^2(i,1) \right]. \quad (\text{A1})$$

The evaluation of the summation in (A1) is performed by utilizing the matrix elements of the effective GF of the infinite system, which are<sup>12</sup>

$$g_e(m, m') = t^{|m-m'|} [2sJ(\xi^2 - 1)^{1/2}]^{-1}, \quad (\text{A2})$$

where

$$t = \xi + s(\xi^2 - 1)^{1/2}, \quad (\text{A3})$$

with

$$s = \pm 1 \text{ so that } |t| < 1. \quad (\text{A4})$$

From Ref. 12, the GF  $G_0$  of the semi-infinite system is given in terms of  $g_e$  via

$$G_0(m, m') = g_e(m, m') \{ 1 + t^p [(c_s - c_b)\Delta + \sigma_s - \sigma_b + Jt] G_0(1,1) \}, \quad (\text{A5})$$

where

$$p = m + m' - |m - m'| - 2, \quad (\text{A6})$$

and  $G_0(1,1)$  is the surface GF (10). Setting  $m = i$ ,  $m' = 1$  in (A6) and (A2) gives, respectively,  $p = 0$  and

$$g_e(i, 1) = t^{i-1} [2sJ(\xi^2 - 1)^{1/2}]^{-1}. \quad (\text{A7})$$

Substituting these into (A5), and performing some algebraic manipulation, leads to

$$G_0(i, 1) = t^{i-1} G_0(1, 1). \quad (\text{A8})$$

Thus,

$$\sum_{i=1}^{\infty} G_0^2(i, 1) = \sum_{i=1}^{\infty} t^{2i-2} G_0^2(1, 1) = G_0^2(1, 1) \sum_{j=0}^{\infty} t^{2j} = G_0^2(1, 1) / (1 - t^2), \quad (\text{A9})$$

where the convergence of the summation is ensured by the fact that  $|t| < 1$  (A4). Inserting (A9) into (A1) results in (33).

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