Chemisorption on binary alloys with long-range order

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The chemisorption properties of a binary alloy of equal concentration with long-range order are studied. The alloy is modeled as a semi-infinite chain of atoms divided into two sublattices, each with different concentrations of the components, thus having a long-range order. The coherent-potential approximation is used to describe the solid with partial disorder and the surface Green's function thus obtained allows the chemisorption process to be treated within the framework of Anderson-Newns theory. The properties of hydrogen chemisorption on an $Ag_{0.5}Cd_{0.5}$ alloy are calculated as functions of the long-range order that is seen to play the role of the surface concentration of the alloy.

I. INTRODUCTION

The problem of chemisorption on disordered binary alloys has been the subject of investigations by several authors.[1-4] The most recent study[4] used the coherent-potential approximation[5] (CPA) to describe the substitutional disorder of the substrate and the Anderson-Newns model[6] to calculate its chemisorption properties. Although those calculations determined the qualitative dependence of the chemisorption energy on the bulk and surface concentrations of the alloy, they did not examine any effects of partial ordering in the solid due to the presence of a long-range order (LRO). The LRO is expected to alter significantly the chemisorption properties of a binary alloy because of the strong effects it is known[7] to have on the densities of states (DOS) of such materials.

The purpose of the present paper, then, is to include the LRO in the theory of chemisorption of atoms or molecules on binary alloys of equal concentration using a model proposed by Foo and Amar[7] (FA). The formalism presented here is applied to a model calculation of the chemisorption of atomic hydrogen on a $Ag_{0.5}Cd_{0.5}$ chain with a variable degree of ordering due to the LRO.

II. FORMALISM

The FA model considers a partially disordered alloy, consisting of two species of atoms of equal concentration. In the pure ordered sample, the solid lattice has two sublattices of alternating sites occupied by A and B atoms with atomic Coulomb energies ε_A and ε_B, respectively. However, because of the disorder, the concentrations of the components are different in the two sublattices, namely C_{iA} and C_{iB}, where $i = 1, 2$ is the sublattice index. This subdivision produces a long-range order (LRO) in the solid defined by the parameter η, via

$$C_{1A} = C_{2B} = 0.5(1 + \eta) \tag{1a}$$

and

$$C_{2A} = C_{1B} = 0.5(1 - \eta) . \tag{1b}$$

Within the single-site coherent-potential approximation (CPA), the true atomic potential on each site of the ith sublattice is represented by a complex energy-dependent CP $\sigma_i(E)$, calculated from a coupled pair of the standard CPA self-consistency conditions,[7]

$$\sigma_1 = \bar{\varepsilon}_1 - (\sigma_1 - \varepsilon_A)(\sigma_1 - \varepsilon_B) g_{11}(\sigma_1, \sigma_2) \tag{2a}$$

and

$$\sigma_2 = \bar{\varepsilon}_2 - (\sigma_2 - \varepsilon_A)(\sigma_2 - \varepsilon_B) g_{22}(\sigma_1, \sigma_2) , \tag{2b}$$

where

$$\bar{\varepsilon}_i = C_{iA}\varepsilon_A + C_{iB}\varepsilon_B . \tag{3}$$

For the infinite one-dimensional nearest-neighbor Hamiltonian

$$H = \sum_n \sigma_n |n\rangle\langle n| + J \sum_n (|n\rangle\langle n+1| + |n+1\rangle\langle n|) \tag{4}$$

(where $\sigma_n = \sigma_i$ for atomic site n on the ith sublattice), the Green's functions (GF's) g_{11} and g_{22} can be shown[8] to be

$$g_{11} = (E - \sigma_2)\Delta^{-1} \tag{5a}$$

and

$$g_{22} = (E - \sigma_1)\Delta^{-1} , \tag{5b}$$

where

$$\Delta = J^2(\alpha^2 - 4)^{1/2} , \tag{6}$$

with

$$\alpha = (E - \sigma_1)(E - \sigma_2)/J^2 - 2 . \tag{7}$$

It should be noted that, for $\eta = 0$, the solid is completely disordered with $\sigma_1 = \sigma_2$, while for $\eta = 1$, it is completely

ordered with $\sigma_1 = \varepsilon_A$ and $\sigma_2 = \varepsilon_B$.

The effect of the presence of the surface on the band structure of the solid is treated by a method first introduced by Kalkstein and Soven[9] for ordered solids and then extended to randomly disordered samples by Berk[10] and others.[11] A surface is created by passing a cleavage plane between the 0 and 1 lattice sites, and modifying the CP on the surface site ($n = 1$) from σ_1 to σ_s. The surface GF G_s is related to the GF of the infinite sample g by the Dyson equation

$$G_s = g + gVG_s \; , \tag{8}$$

where the cleavage potential is

$$V = (\sigma_s - \sigma_1)|1\rangle\langle 1| - J(|1\rangle\langle 0| + |0\rangle\langle 1|) \; . \tag{9}$$

Some algebraic manipulations (cf. Refs. 10 and 11) lead to

$$G_s(1,1) = [g_{11}^{-1} - \sigma_s + \sigma_1 + J^2(E - \sigma_2)^{-1}(z+1)]^{-1} \; , \tag{10}$$

where

$$z = [\alpha \mp (\alpha^2 - 4)^{1/2}]/2, \quad |z| < 1 \; . \tag{11}$$

The surface CP σ_s is calculated from a condition, similar to (2), to be

$$\sigma_s = \frac{\{\overline{\varepsilon}_1[g_{11}^{-1}(1-z)^{-1} + \sigma_1] - \varepsilon_A \varepsilon_B\}}{[g_{11}^{-1}(1-z)^{-1} + \sigma_1 + \overline{\varepsilon}_1 - (\varepsilon_A + \varepsilon_B)]} \; . \tag{12}$$

During the process of chemisorption, an atom of atomic energy ε_a is adsorbed onto the end atom of the semi-infinite chain by a bond of energy γ. The presence of the adatom at the surface perturbs the surface CP from σ_s to σ_c. The chemisorption process itself is taken to occur according to the Anderson-Newns[6] model, within the restricted Hartree-Fock approximation, in which ε_a is shifted upwards by an amount $v = U\langle n_a \rangle$, where U is the intra-atomic Coulomb repulsion on the adatom and $\langle n_a \rangle$ is the expected single-spin occupancy of the adatom after chemisorption. Hence the Dyson equation

$$G_a = G_s + G_s V_a G_a \; , \tag{13}$$

with perturbation potential

$$V_a = v|0\rangle\langle 0| + \gamma(|0\rangle\langle 1| + |1\rangle\langle 0|) + \delta|1\rangle\langle 1| \; , \tag{14}$$

where

$$\delta = \sigma_c - \sigma_s \; , \tag{15}$$

can be used to calculate the GF, on the adatom site, to be

$$G_a(0,0) = \{E - \varepsilon_a - v - \gamma^2[G_s^{-1}(1,1) - \delta]^{-1}\}^{-1} \; . \tag{16}$$

A self-consistency condition for σ_c, equivalent to (2), can be shown to yield the explicit expression

$$\sigma_c = \{\overline{\varepsilon}_1 f(E) - \varepsilon_A \varepsilon_B\}/[f(E) - (\varepsilon_A + \varepsilon_B) + \overline{\varepsilon}_1] \; , \tag{17}$$

where

$$f(E) = G_s^{-1}(1,1) + \sigma_s - \gamma^2(E - \varepsilon_a - v)^{-1} \; . \tag{18}$$

When chemisorption occurs, charge transfer takes place between the adatom and the substrate, with the final electronic occupancy of the adatom orbital $|0\rangle$ being given by

$$\langle n_a \rangle = \int_{-\infty}^{\varepsilon_F} \rho_a(E) dE \; , \tag{19}$$

where ε_F is the Fermi energy, and the adatom DOS is

$$\rho_a(E) = -\pi^{-1} \mathrm{Im} G_a(0,0) \; . \tag{20}$$

The actual evaluation of (19) requires that the integral be broken into the integrals over the occupied band states, plus the residues of the poles of $G_a(0,0)$, which correspond to localized states. It is clear from (16), (19), and (20) that $\langle n_a \rangle$ is dependent upon the chemisorption CP σ_c, which, in turn, is itself a function of $\langle n_a \rangle$, via (17) and (20). Thus there is a self-consistent coupling of the quantities $\sigma_c(E)$ and $\langle n_a \rangle$.

Using the Dyson equations (8) and (13), the change $\Delta\rho$ in the total DOS caused by chemisorption can be shown to be

$$\Delta\rho(E) = -\pi^{-1} \mathrm{Im} \left[\sum_{n=0}^{\infty} [G_a(n,n) - G_s(n,n)] \right]$$

$$= -\pi^{-1} \mathrm{Im}(v[G_s(0,0)]^2[1 - \delta G_s(1,1)] + \gamma^2[G_s(0,0)]^2 G_s(1,1)$$

$$+ \{\gamma^2 G_s(0,0) + \delta[1 - v G_s(0,0)]\}[G_s(1,1)]^2(1-z^2)^{-1}[1 + J^2(E - \sigma_2)^{-2}(1+z)^2])/M \; , \tag{21}$$

where

$$G_s(0,0) = (E - \varepsilon_a)^{-1} \; , \tag{22}$$

and

$$M = [1 - v G_s(0,0)][1 - \delta G_s(1,1)] - \gamma^2 G_s(0,0) G_s(1,1) \; . \tag{23}$$

The chemisorption energy can then be written as[4]

$$\Delta E = 2\Delta E^{1\sigma} - U(\langle n_a \rangle)^2 + \varepsilon_a - E_{p3} \; , \tag{24}$$

where the one-electron energy change is

$$\Delta E^{1\sigma} = \sum_{i=1}^{3} (E_{pi} - E_{zi}) + \int_{\varepsilon_{l1}}^{\varepsilon_{u1}} E \, \Delta\rho(E)dE$$

$$+ \int_{\varepsilon_{l2}}^{\varepsilon_{u2}} E \, \Delta\rho(E)dE \ . \tag{25}$$

In the above, E_{pi} (E_{zi}) is a pole (zero) of $G_a(0,0)$, of which there is a maximum of three of each sort for the system under consideration, and ε_{li} (ε_{ui}) is the lower (upper) edge of the ith energy band in a persistent alloy. Finally, the charge transfer from the substrate to the adatom is

$$\Delta q/e = 2\langle n_a \rangle - 1 \ . \tag{26}$$

III. RESULTS AND DISCUSSION

For the purpose of numerical calculations, the chemisorption of atomic H on $Ag_{0.5}Cd_{0.5}$ was modeled. The substrate parameters, measured from the vacuum level, were taken to be $\varepsilon_A = -10.3$ eV, $\varepsilon_B = -15.85$ eV, $\varepsilon_F = -4.3$ eV, and $J = 1.1$ eV and were chosen so as to produce the best possible agreement with the actual persistent-type band structure of the totally disordered alloy.[12] A self-consistent calculation of the density of states was performed, with these parameters being concluded to be the ones most suitably reproducing the experimental positions of the band edges of disordered $Ag_{0.5}Cd_{0.5}$. The band edges ε_{li} and ε_{ui} needed in (25) were calculated self-consistently using the CPA. These parameters are simply σ_1, σ_2 and

$$\pm((\sigma_1+\sigma_2)/2 + \{[(\sigma_1+\sigma_2)/2]^2 + 4J^2\}^{1/2}) \ .$$

ε_A represents Ag, and hence γ was assumed to have the value for pure Ag, namely 4.836 eV, which was evaluated by means of a tight-binding Anderson-Newns calculation on the pure substrate. The parameters[6] for H are $\varepsilon_a = -14.3$ eV and $U = 12.9$ eV.

The graph of chemisorption energy ΔE versus the LRO parameter η is given in Fig. 1. The curve shows clearly that ΔE is monotonically (nearly linear) increasing with LRO, corresponding to weaker chemisorption. The
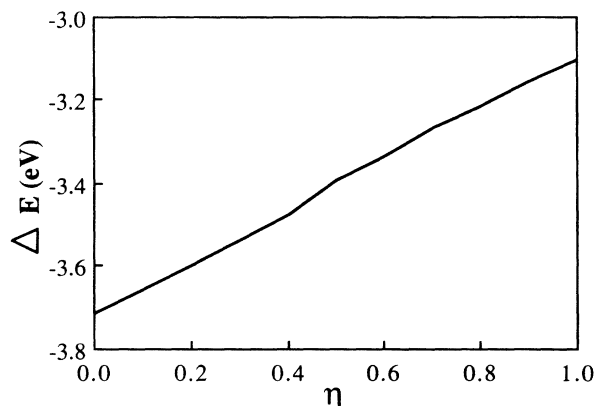
results are not unexpected in light of the fact that the calculated ΔE for the ordered substrate with Cd on the surface is -4.36 eV, as compared to -3.11 eV when Ag is the surface atom. Ag, then, is the weaker-binding element, so an increase in LRO produces a larger probability of Ag being the surface atom, and hence the increase in ΔE. On the other hand, changing the LRO in such a way so that Cd is the more probable surface atom should decrease ΔE towards -4.36 eV. Thus, it is concluded that η, in effect, acts like a surface concentration, and its variation produces behavior of the sort seen on plots of ΔE versus concentration, for other alloy systems.[4] As a consequence, it comes as no surprise that ΔE for the totally disordered substrate is approximately the average of the values for the two possible ordered substrates.

For the realistic three-dimensional situation, the totally ordered solid would possess a surface layer containing equal numbers of Ag and Cd atoms for a simple cubic lattice. In the absence of any preferential adsorption, the average chemisorption energy would be approximately the mean of those for the two possible one-dimensional cases, i.e., ~ -3.74 eV. At first, this value would seem to be very close to what would be expected for the disordered substrate, namely -3.71 eV. However, any surface segregation occurring in disordered Ag/Cd would perturb the surface concentration from 50-50, and as a result, could shift ΔE significantly away from -3.71 eV. Thus LRO would still be expected to play an important role in the chemisorption process.

The charge transfer Δq (in units of e) as a function of η (Fig. 2) shows that an increase in charge transfer to the adatom corresponds to stronger chemisorption. Indeed, for values of η close to 1, Δq is negative, so that the charge distribution of the chemisorption bond is more localized on the surface atom of the substrate.

Localized chemisorption state energies E_{pi} calculated from the poles of $G_a(0,0)$ (see Table I) exhibit a monotonically decreasing dependency on η. Except for the ordered solid ($\eta=1$), there are always three such states, one each below the bands, above them and in the band gap. This behavior would appear on first thought to contradict the trend in ΔE, shown in Fig. 1, but it must be noticed that in (25) the relevant quantities are the differences

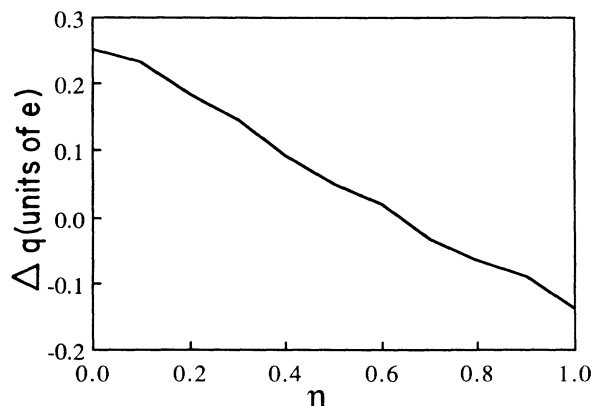FIG. 1. Chemisorption energy ΔE vs η for H-Ag/Cd (in eV).

FIG. 2. Charge transfer Δq vs η for H-Ag/Cd (in units of e).

TABLE I. Chemisorption state energies (in eV), measured from vacuum level.

η	E_{p1}	E_{p2}	E_{p3}
0.0	−18.21	−13.45	−4.19
0.1	−18.24	−13.46	−4.30
0.2	−18.29	−13.53	−4.56
0.3	−18.33	−13.58	−4.77
0.4	−18.39	−13.67	−5.06
0.5	−18.43	−13.74	−5.29
0.6	−18.47	−13.78	−5.45
0.7	−18.53	−13.88	−5.72
0.8	−18.57	−13.94	−5.89
0.9	−18.60	−13.98	−6.02
1.0		−14.08	

$E_{pi} - E_{zi}$, which are increasing functions of η. The state E_{p2}, whose energy is located in the band gap, is the shifted hydrogen level ε_a, while the other two are one-time band states, which have been removed from the bands by the chemisorption-induced perturbation of the surface CP. The fact that the latter two states do not appear for the ordered case is evidence of the influence of disorder on their origins.

IV. SUMMARY AND CONCLUSION

The effect of long-range order on the chemisorption properties of a disordered binary alloy of equal concentration has been studied using the Anderson-Newns model for chemisorption. The GF for the infinite disordered sample with LRO has been calculated within the single-site CPA using the method of FA. The surface GF for the disordered sample has then been obtained by the method of Berk.

Numerical calculations for the chemisorption energy ΔE and charge transfer Δq have been performed for chemisorption of a hydrogen atom on the $Ag_{0.5}Cd_{0.5}$ alloy with the LRO parameter varying from $\eta = 1.0$ (completely ordered) to $\eta = 0$ (completely disordered.) ΔE and Δq are observed to be monotonic functions of the LRO parameter η. From the calculated results it can be surmised that the LRO effectively controls the concentration at the surface, which is a key parameter in determining the chemisorption behavior of the alloy. Hence an increase in the surface concentration of the component with greater chemisorption ability produces stronger chemisorption on the alloy.

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