Chemisorption of Ordered Overlayer on a Tight-Binding Metal Surface Two-Level Adsorbate

K. Masuda

Department of Materials Science and Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan

Z. Naturforsch. **37a**, 1147–1157 (1982); received April 21, 1982

The chemisorption of a two-level (at E_1 and E_2) adsorbate on the (001) surface of a tight-binding metal is investigated using the Green's function formalism and the phase shift technique. The adorbital density of states (DOS)$\varrho_a(E)$ as well as the change in the electronic DOS $\Delta\varrho(E; E_1, E_2)$ due to chemisorption are calculated for the ordered overlayers with $c(2\times2)$, $p(2\times1)$, $p(2\times2)$, $p(4\times1)$ and $c(4\times2)$ structures. It is assumed that the chemisorbed species sit over the twofold bridge site of the (001) surface of the model transition metal and have a π-bonding interaction with the two substrate atoms. It is shown that the electronic states of the overlayers are very sensitive to the adsorbate coverage (θ), adsorbate structure and adsorbate species (one level or two level adsorbates). Furthermore, it is shown that there are marked differences in the $\Delta\varrho(E)$ curves between the chemisorption of two level adsorbates $\Delta\varrho(E; E_1, E_2)$ and that of single level adsorbates $\Delta\varrho(E; E_1) + \Delta\varrho(E; E_2)$ (simulating the changes in the electronic DOS during the dissociation of diatomic molecules).

1. Introduction

One of the main subjects in the study of chemisorption is concerned with the interaction between adsorbate atoms or molecules on metal surfaces. The surface superstructures are formed due to lateral interactions between adsorbed species and have been observed in many chemisorption systems by low energy electron diffraction (LEED) [1, 2]. On the other hand, vibrational frequency shift of adsorbed species also arises from the adsorbate interactions [3]. Grimley [4] and Einstein and Schrieffer [5], using a model calculation, have investigated the indirect interaction between pairs of adatoms on a metal surface. The theory has also been applied to ordered overlayers with general coverage $\theta(<1.0)$ by several authors [6–8]. In this type of model calculation, the adatoms are assumed to have a single sharp energy level E_a which couples to the host atoms with hopping interactions V_{as} and V_{sa}.

It is the purpose of the present paper to investigate the interaction between adsorbed species using a more general chemisorption model: We use a two level adsorbate on a tight-binding (TB) metal surface, which is applicable to di-atomic molecules like NO, CO, etc. on transition metal (TM) surfaces. Recent experimental and theoretical work has been concerned with the adsorption or dissociation of di-atomic molecules on TM surfaces. In particular, CO (or NO)/TM systems are of great interest [9]. Quite recently Gorte and Schmidt [10] have studied the interactions between CO and NO molecules adsorbed on a TM (Pt) surface. Kiskinova [11] has investigated the effects of having electropositive (alkali) adatoms on the dissociation of di-atomic molecules like CO. Plummer [12], and Semancik and Estrup [13] used the photoelectron spectra from CO adsorbed TM surface to identify the adsorbate states, i.e., molecule or dissociated states.

To investigate the electronic structure of chemisorbed layers, we treat the dilute ordered overlayers with coverages $\theta = 1/4$ and $1/2$ rather than the pair of adsorbates, since this kind of superstructure has been frequently observed for di-atomic molecule/TM systems [1]. We consider two-level adsorbate having a π-bonding interaction with the s-orbitals on the two substrate atoms at the bridge site of a simple cubic (sc) (100) metal surface (Figure 1). The two π-bonds in this geometry are assumed to be degenerate (adding the interaction between them would mix and split the two states) [14, 15]. For comparison, we also consider the one-level adsorbate having a π-bonding interaction with the substrate orbitals. This enables us to understand the effects of having two-level (π-bonding) adsorbates on a metal surface and is useful to simulate the changes

Reprint requests to Herrn Dr. K. Masuda, Department of Materials Science and Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan.

0340-4811 / 82 / 1000-1147 $ 01.30/0. — Please order a reprint rather than making your own copy.

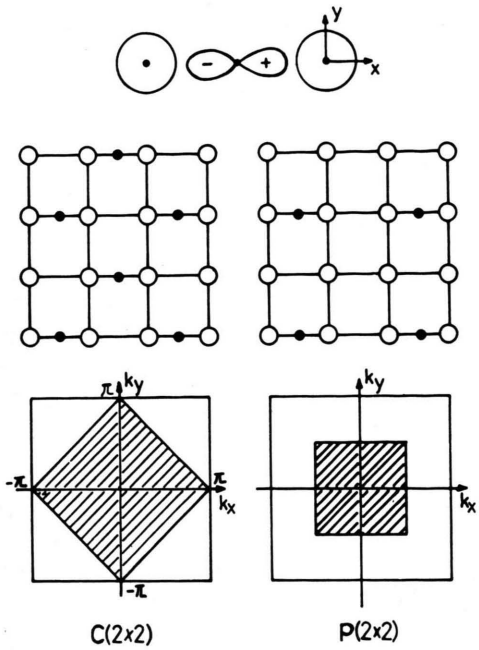

Fig. 1. Geometry of the π-bonding adsorption over the bridge-site on the sc(001) surface Also shown are the first ABZ (hatched region).

in the electronic density of states (DOS) during the dissociation of adsorbed species.

Following Cunningham et al. [15], we introduce two types of twolevel adsordates; for case A adsorbate, one orbital is coupled directly to the substrate atoms and another orbital is not coupled to the substrate directly but has a direct interaction with the first adsorbate level. In contrast, for case B two levels are bonded individually to the substrate, but there is no explicit coupling between these two levels. The present model does not contain explicitly the electron-electron interaction (correlation) effects on the adsorbate in contrast to the usual Newns-Anderson model [2]. This treatment, however, seems to be sufficient for the qualitative understanding of chemisorption behaviour.

We calculate the adorbital DOS $\varrho_a(E)$ as well as the change in the DOS during chemisorption $\Delta\varrho(E)$ using the Green's function formalism and the phase shift technique [16]. The main advantage of the phase shift technique is that it provides directly the changes in the electronic DOS during chemisorption. This information is quite important since it is directly applicable to photoemission. No other method gives this information in such a straightforward manner.

In Sect. 2, we present the principle of calculations for obtaining the chemisorbed Green's function and the change in the electronic DOS due to chemisorption of the dilute overlayers with $\theta = 1/4$ and $1/2$ (extension to other type overlayers is straightforward). Results of numerical calculations and the related discussions are given in Section 3. The final Sect. 4 is devoted to conclusions.

2. Principle of Calculations

The binding of a diatomic molecule like CO to a metal surface takes place through electron transfer from the occupied σ orbital (5σ) to the metal and by backdonation of metallic electrons into the empty antibonding π^* orbital (doubly degenerate $2\pi^*$ orbital). To simulate electronic state of the diatomic molecule on a TM surface, we introduce a two-level adsorbate having a π-bonding interaction with the sc(100) tight-binding substrate. Similar model has been used with some success to investigate the admixture interaction between the two adorbitals [15].

The bonding interaction between the substrate atoms and the adsorbate is described by a one-electron hopping parameter (see the Appendix). The Kalkstein and Soven approach [17] is used to calculate the clean surface Green's function. This approach uses the linear combination of atomic orbital (LCAO) scheme, which gives the energy band expression of the bulk crystal

$$E_k = E_0 + 2t[\cos(k_x) + \cos(k_y) + \cos(k_z)], \quad (1)$$

where $t(E_0)$ denotes the nearest-neighbour transfer integral (substrate atomic level). Solving the Dyson equation (mixed Bloch-Wannier representation), one can derive the explicit expression for the surface Green's function $G_0^s(k_x, k_y; n, E)$, where (k_x, k_y) $[\equiv k_\parallel]$ denotes the wave vector parallel to the surface and n lavels the n-th atomic layer [16]. To calculate the change in the electronic DOS $\Delta\varrho(E)$ upon chemisorption, we use a phase-shift technique [16]. This method is very powerful (exact within one electron approximation) and has been applied to wide variety of solid state physics problems such as surface reconstruction [18], bimetallic interface [19] and metal-semiconductor junctions [20].

The change in the electronic DOS $\Delta\varrho(E)$ can be calculated from the phase-shift function $\eta(k_\parallel; E)$

which is written as

$$\eta_\chi(k_\parallel; E) = -\operatorname{Arg}\det[\tilde{I} - \tilde{V}_x \cdot \tilde{G}_0(k_\parallel; E)]\,, \quad (2)$$

where $\tilde{I}$ is the identity matrix, and $\tilde{V}$ and $\tilde{G}_0$ are the perturbation and unperturbed Green's function matrices, respectively. $\tilde{V}$ and $\tilde{G}_0$ depend on the binding geometry of ordered overlayers, through the reciprocal lattice vectors K_h of the overlayers [6, 7]. Here, it is important to note that for a given wave vector $k_\parallel$ in the adsorbate first Brilluoin Zone (ABZ), there are $q k_\parallel^s$ (q times of $k_\parallel$) in the surface Brillouin Zone (SBZ) that are expressed as $k_\parallel^s = k_\parallel + K_h$, where $q = 2(4)$ for the overlayers with coverage $\theta = 1/2\,(1/4)$ [6, 7].

Once the $k_\parallel$ dependent phase-shift function $\eta_\chi(k_\parallel; E)$ is known, it is straightforward to calculate the change in the electronic DOS upon chemisorption from

$$\Delta\varrho(E) = \frac{1}{\pi}\,\partial\eta_\chi(E)/\partial E\,, \quad (3)$$

where the total phase shift junction $\eta_\chi(E)$ is defined by

$$\eta_\chi(E) = \Big\{(1/N_a)\sum_{k_x, k_y}\eta_\chi(k_x, k_y; E) - \sum_i \pi\,\theta(E_i - E)\Big\}\,. \quad (4)$$

Here, N_a denotes the number of adsorbate species, the summation of k_x and k_y extends over the first ABZ and the Heaviside theta function is added so that $\Delta\varrho(E)$ directly gives the difference in the DOS between the chemisorbed system and the clean substrate. In Eq. (3) we find the sum rule for the two level adsorbate species

$$\int_{-\infty}^{+\infty}\Delta\varrho(E)\,\mathrm{d}E = 2\,, \quad (5)$$

since we are adding two electron states per adsorbate to the system. Furthermore, $\Delta\varrho(E)$ in Eq. (3) is the quantity of experimental interest since photoemission difference spectra are obtained by subtraction of the clean substrate spectrum from the total chemisorbed system spectrum.

The adsorbate electronic DOS $\varrho_a(E)$ can be obtained as follows. The adsorbate Green's function $G_{aa}(k_\parallel; E)$ can be obtained by solving the matrix form Dyson equation $G = \tilde{G}_0 + \tilde{G}_0\,\tilde{V}\,\tilde{G}$ [6, 7]. After a bit of algebra and noting the relation among wave vectors $k_\parallel$, $k_\parallel^s$ and K_h, one can obtain the explicit expression for $G_{aa}^0(k_\parallel; E)$ function. In a mixed Bloch-Wannier representation $G_{aa}^0(k_\parallel; E)$ can be given as

$$G_{aa}(k_\parallel; E) = \Big[G_{aa}^{0\,-1} - \sum_{K_h} V_h^2 G_{ss}^0(k_\parallel + K_h, E)\Big]^{-1}\,, \quad (6)$$

where G_{aa}^0 represents the unperturbed adsorbate Green's function. Then one can calculate the adorbital DOS $\varrho_a(E)$ by the usual formula

$$\varrho_a(E) = -(1/\pi N_a)\,\mathrm{Im}\sum_{k_x, k_y} G_{aa}(k_\parallel; E)\,, \quad (7)$$

where the sum is over the first ABZ.

2.1. *One-Level π-Bonding Chemisorption*

In this subsection, we consider the one-level (at energy E_1) π-bonding chemisorption on the sc(001) TB metal surface. We give, as an example, the explicit expression of $G_{aa}(k_\parallel; E)$ for the $p(2\times 1)$ overlayer. The extension to other type overlayers is straightforward. For the $p(2\times 1)$ overlayer with $K_h = (0, 0)$ and $(-\pi/a, 0)$, the adsorbate Green's function $G_{aa}(k_\parallel; E)$ can be given as

$$G_{aa}(k_\parallel; E) = [E - E_1 - \tfrac{1}{2}V_1^2\{4\sin^2(k_x/2)\,G_{ss}^0(k_x, k_y; E) + 4\cos^2(k_x/2)\,G_{ss}^0(\pi - k_x, k_y; E)\}]^{-1}\,, \quad (8)$$

where factors $4\sin^2(k_x/2)$ and $4\cos^2(k_x/2)$ are due to the bridge site π-bonding adsorption. V_1 is the coupling strength (one electron hopping parameter) between the adorbital and the substrate atom orbital. Here, we neglect the overlap of the adsorbate and substrate wave functions. On the other hand, $k_\parallel$ dependent phase-shift function $\eta_\chi(k_\parallel; E)$ can be given as

$$\eta_\chi(k_\parallel; E) = -\operatorname{Arg}[1 - \tfrac{1}{2}V_1^2\{4\sin^2(k_x/2)\,G_{ss}^0(k_x, k_y; E) + 4\cos^2(k_x/2)\,G_{ss}^0(\pi - k_x, k_y; E)\}\,G_{aa}^0(E)]. \quad (9)$$

2.2. *Two-Level Chemisorption: Case A*

Following Cunningham et al. [15], we consider the adsorbate having two (free gas phase) energy levels E_1 and E_2, where the level at E_1 is coupled to each substrate atom with strength V_1, and the level at E_2 is coupled to the first level with strength V_c due to surface-induced rehybridization. As in Subsec. 2.1 we present the explicit expressions of adsorbate Green's function for the $p(2\times 1)$ overlayer: The adsorbate Green's function $G_{aa}(k_\parallel; E)$

can be given for the adorbital 1 (at the energy E_1) as

$$G^{(1)}_{aa}(k_\parallel; E) = [E - E_1 - \tfrac{1}{2} V_1^2 \{4\sin^2(k_x/2)\, G^0_{ss}(k_x, k_y; E) + 4\cos^2(k_x/2)\, G^0_{ss}(\pi - k_x, k_y; E)\} - V_c^2/(E - E_2)]^{-1}, \quad (10)$$

while for the adorbital E_2

$$G^{(2)}_{aa}(k_\parallel; E) = [E - E_2 - V_c^2/\{E - E_1 - \tfrac{1}{2} V_1 (4\sin^2(k_x/2)\, G^0_{ss}(k_x, k_y; E) + 4\cos^2(k_x/2)\, G^0_{ss}(\pi - k_x, k_y; E)\}]^{-1}. \quad (11)$$

The $k_\parallel$ dependent $\eta_\chi(k_\parallel : E)$ can be obtained in a similar manner.

2.3. *Two-Level Chemisorption: Case B*

For the type B adsorbate, we consider the two levels at E_1 and E_2 to be coupled to the substrate orbitals with hopping interactions V_1 and V_2, respectively. The $p(2\times 1)$ chemisorbed Green's functions for adorbitals at E_1 and E_2 are given, respectively, as

$$G^{(1)}_{aa}(k_\parallel; E) = [Z_1(k_\parallel; E) - \tfrac{1}{4} V_1^2 V_2^2 \{4\sin^2(k_x/2)\, G^0_{ss}(k_x, k_y; E) + 4\cos^2(k_x/2)\, G^0_{ss}(\pi - k_x, k_y; E)\}^2 / Z_2(k_\parallel; E)]^{-1}, \quad (12)$$

$$G^{(2)}_{aa}(k_\parallel; E) = [Z_2(k_\parallel; E) - \tfrac{1}{4} V_1^2 V_2^2 \{4\sin^2(k_x/2)\, G^0_{ss}(k_x, k_y; E) + 4\cos^2(k_x/2)\, G^0_{ss}(\pi - k_x, k_y; E)\}^2 / Z_1(k_\parallel; E)]^{-1}, \quad (13)$$

where $Z_1(k_\parallel; E)$ and $Z_2(k_\parallel; E)$ are

$$Z_1(k_\parallel; E) = E - E_1 - \tfrac{1}{2} V_1^2 \{4\sin^2(k_x/2)\, G^0_{ss}(k_x, k_y; E) + 4\cos^2(k_x/2)\, G^0_{ss}(\pi - k_x, k_y; E)\}, \quad (14)$$

$$Z_2(k_\parallel; E) = E - E_2 - (V_2^2/2)\{4\sin^2(k_x/2)\, G^0_{ss}(k_x, k_y; E) + 4\cos^2(k_x/2)\, G^0_{ss}(\pi - k_x, k_y; E)\}. \quad (15)$$

Again, the $k_\parallel$ dependent phase-shift function $\eta_\chi(k_\parallel; E)$ can be obtained in a similar manner (Equation (9)).

3. Numerical Results and Discussions

In this section, we present the numerical results of adorbital DOS $\varrho_a(E)$ and $\Delta\varrho(E)$ during chemisorption for the $c(2\times 2)$, $p(2\times 1)$, $p(2\times 2)$ and $p(4\times 1)$ overlayers. In Fig. 2 we show the chemisorption function [15], both real (dashed) and imaginary (solid curve) parts, for bridge-site π-bonding adsorption on the sc(001) TB metal surface. Though this choice for substrate does not allow quantitative statements about the fivefold degenerate d-band of bcc or fcc transition metals, it yields the simple broad DOS structure one would like the substrate to present in a model calculation, compared for instance to s-band bcc or fcc crystal. Allan [21], Einstein and Schrieffer [5] and other authors [22] have used this substrate to study chemisorption and chemisorption related phenomena on transition metal surfaces.

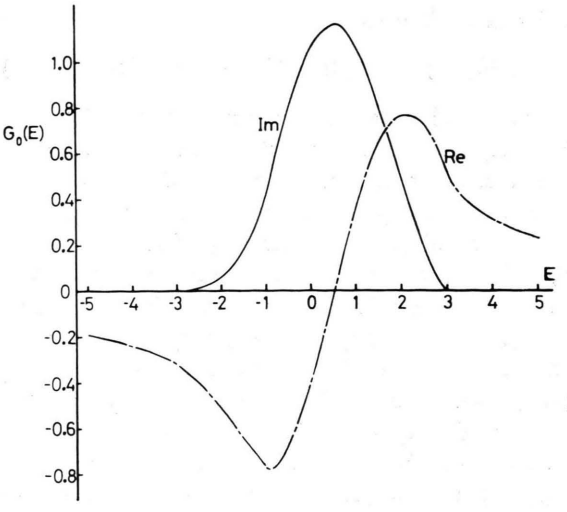

Fig. 2. The imaginary (solid) and real (dot-dashed curve) parts of the π-bonding Green's function for the substrate group orbital of the symmetry (projected onto one of the two substrate sites) of Figure 1.

3.1. *Two-Level Chemisorption: Case A*

In the present numerical calculation substrate atomic level is set equal to zero, and energy is given in units of $2|t|$. To relate our model to actual crystals, we assume that $2|t| \approx 1.6$ eV. This gives a substrate band width of 9.6 eV. We choose an unperturbed adsorbate levels E_1 and E_2 within the substrate band; E_1 and E_2 are 1.2 (1.92 eV) and -0.7 (-1.12 eV), respectively. The hopping parameter V_1 between the adsorbate level E_1 and each substrate atom is chosen to be 1.2 (1.92 eV). This V_1 value corresponds to a total bond strength $1.2\cdot\sqrt{2}$ (3.1 eV) and belongs to the strong chemisorption regime. On the other hand, the coupling strength V_c between the two adsorbate levels E_1 and E_2 (due to surface-induced rehybridization) is taken as

$V_c = 1/2\, V_1$. These parameter values are similar to those used by Doyen and Ertl [14] and by Cunningham et al. [15].

In Fig. 3 we present the $\Delta\varrho(E)$ curves for the $c(2\times 2)$, $p(2\times 1)$, $c(4\times 2)$, $p(2\times 2)$ and $p(4\times 1)$ overlayers, together with that for the single (isolated) adsorbate (Figure 3a). In general, the change in the electronic DOS $\Delta\varrho(E)$ depends strongly on the type of the overlayers: It is noted that the shapes of the bonding and anti-bonding resonance peaks are quite sensitive to the structure of the overlayers. This indicates that the indirect interactions between the adsorbate species (with two levels) are important in determining the electronic structure of the chemisorbed layers.

For $\Delta\varrho(E)$ curves in Figs. (3a), (e), (d) and (f), one observes three resonance peaks I, II and III, from lowest to highest energy: the fine structures (dip) of the highest resonance III in Figs. 3(d), (e) and (f) arises from the long range order of the overlayers (absent for the isolated adsorbate DOS in Figure 3(b)). The appearance of these three resonances is interpreted as follows. The lowest resonance I is bonding on all orbitals, while the middle resonance II is anti-bonding for orbitals (1) and (2), but bonding between orbital (1) and the substrate orbital. Resonance III is anti-bonding between orbital (1) and the substrate.

In contrast, for the $c(2\times 2)$ and $c(4\times 2)$ overlayers, there appears an additional peak in the $\Delta\varrho(E)$ curves. In order to understand the physical origin for the appearance of the additional resonance peak, we have calculated the adorbital DOS and presented the results in Figure 4. As shown in Fig. 4d ($c(2\times 2)$ overlayer), the lower resonance of the adorbital DOS $\varrho_a^{(1)}(E)$ (for adorbital E_1) splits into two peaks around the adsorbate level E_2. This splitting of the lower resonance peak results from the indirect interactions between the adsorbate species of the particular type ($c(2\times 2)$) ordered overlayers, and is not observed for the adorbital DOS of the isolated adsorbate.

On the other hand, the additional resonance peak near the energy $E\approx 0.8$ for the $c(4\times 2)$ overlayer arises mainly from the adorbital 1 (at E_1) and is also seen in the corresponding $c(4\times 2)$ $\Delta\varrho(E)$ curve of the single-level adsorbates (Figure 6). The appearance of this resonance peak is due to the existence of the wave vector dependent "localized" or "virtual" states associated with the particular type ordered overlayers, fully discussed in our previous report [23]. We have also calculated the change in the DOS $\Delta\varrho(E)$ as well as the adorbital DOS, using another set of parameter values (increasing V_c from $V_1/2$ to V_1). We have found that the qualitative features of the chemisorption behaviour remain almost unchanged, and the indirect interactions between adsorbate species are also important for determining the electronic states of the chemisorbed layers. This indicates that the qualitative conclusions do not depend on the particular choice of the parameter values.

3.2. Two-Level Chemisorption: Case B

We choose an unperturbed adsorbate levels E_1 and E_2 within the substrate band: For comparison with the previous subsection 3.1, $E_1 = 1.2$ (1.92 eV) and $E_2 = -0.7$ (-1.12 eV) are used. The hopping parameter V_2 between the adsorbate level E_2 and each substrate atom is varied from 0 to 1.2 (1.92 eV), while the hopping parameter V_1 is fixed at 1.2 (1.92 eV). The value of 1.2 (1.92 eV) corresponds to a total bond strength $1.2\sqrt{2}$ (3.1 eV).

In Fig. 5, we present the change in the electronic DOS $\Delta\varrho(E)$ during chemisorption for the $c(2\times 2)$ and $p(2\times 1)$ overlayers ($\theta = 0.5$), together with the corresponding $\Delta\varrho(E)$ curves for the isolated (single) adsorbate ($\theta\approx 0$). The hopping parameter V_2 is chosen 0.4 (0.64 eV) for Figs. 5(a), (c) and (e), and 1.2 (1.92 eV) for 5(b), (d) and (f). In Fig. 5 one can observe that $\Delta\varrho(E)$ curve for the $c(2\times 2)$ overlayer is quite different from those for the $p(2\times 1)$ overlayer (in spite of the same adsorbate coverage) and for the single (isolated) adsorbate. This means that the indirect interactions between chemisorbed species (with two levels) play an important role in determining the electronic states of the ordered overlayers. In other words, this indicates the importance of substrate (band structure) contribution to the chemisorption of the two-level adsorbates. Therefore, the approximation of using a single δ-function level for the substrate d states seems to be poor for this kind of problem. Here, it is interesting to note that this effect (importance of the indirect interactions) is rather pronounced for the weak coupling case of $V_2 = 0.4$, as shown in Figs. 5(a), (c) and (e).

We have also calculated $\Delta\varrho(E)$ curves for the $p(4\times 1)$, $p(2\times 2)$ and $c(4\times 2)$ overlayers ($\theta = 1/4$) and presented the results in Fig. 6; $V_2 = 0$ is used

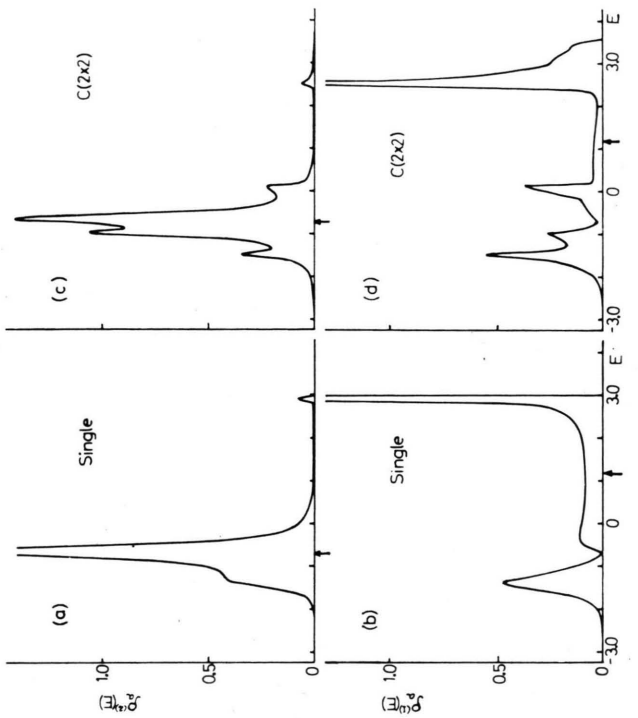

Fig. 3. The change in the electronic DOS $\Delta\varrho(E)$ during the adsorption of the $c(2\times2)$, $p(2\times1)$, $c(4\times2)$, $p(2\times2)$ and $p(4\times1)$ overlayers. $V_1 = 1.2$, $V_c = 0.6$, $E_1 = 1.2$ and $E_2 = -0.7$ (case A adsorbates) are used. Arrows indicate the adsorbate energy levels E_1 and E_2.

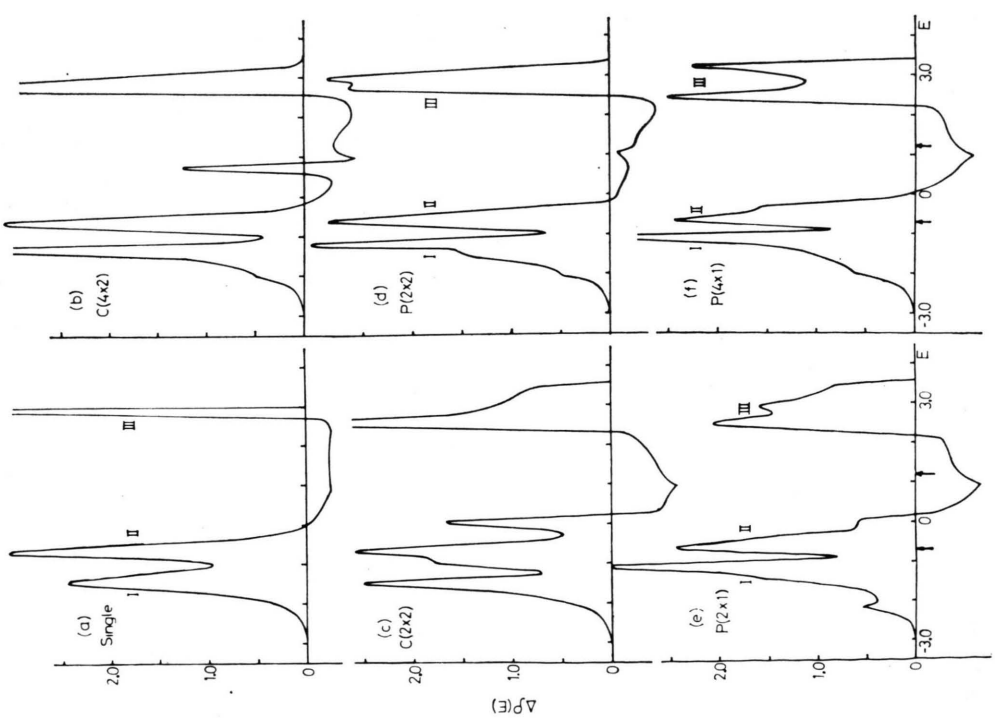

Fig. 4. Adorbital DOS $\varrho_a(E)$ for the $c(2\times2)$ overlayer and for the isolated ($\theta \approx 0$) adsorbates. Parameters are the same as in Figure 3.

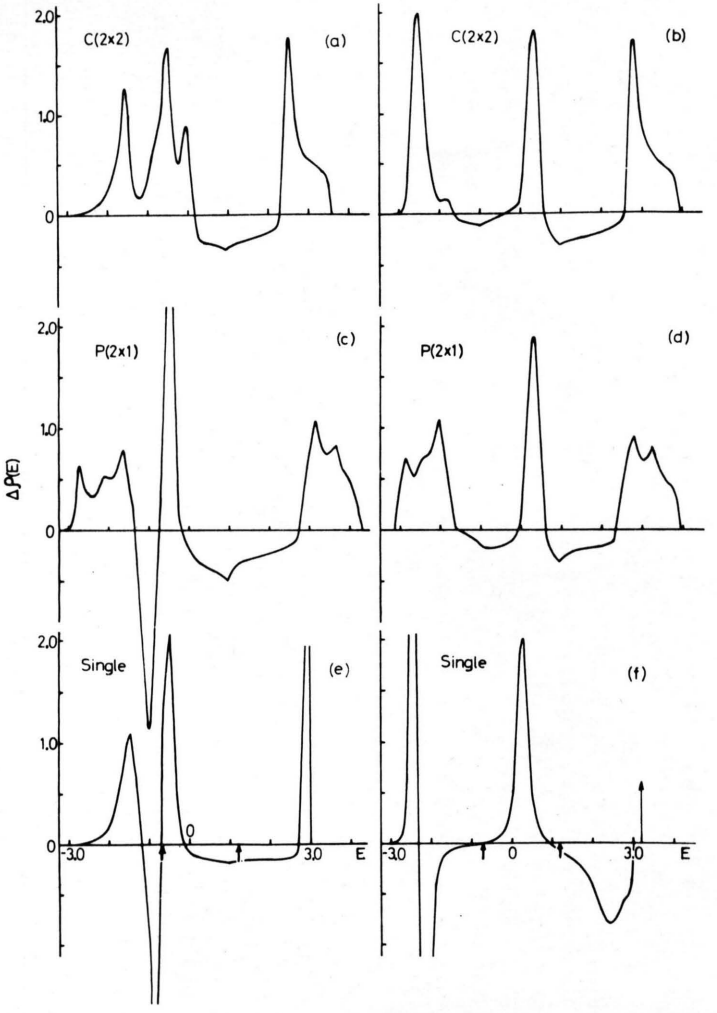

Fig. 5. The change in the electronic DOS $\Delta\varrho(E)$ during the adsorption of the $c(2\times 2)$ and $p(2\times 1)$ overlayers (case B). $E_1 = 1.2$, $E_2 = -0.7$ $V_1 = 1.2$, $V_2 = 0.4$ (5a, 5c and 5e) and $V_2 = 1.2$ (5b 5d and 5f) are used. Also shown is the $\Delta\varrho(E)$ curve for the isolated adsorbate ($\theta \approx 0$): Split-off state (near $E = 3.2$) appears above the upper band edge.

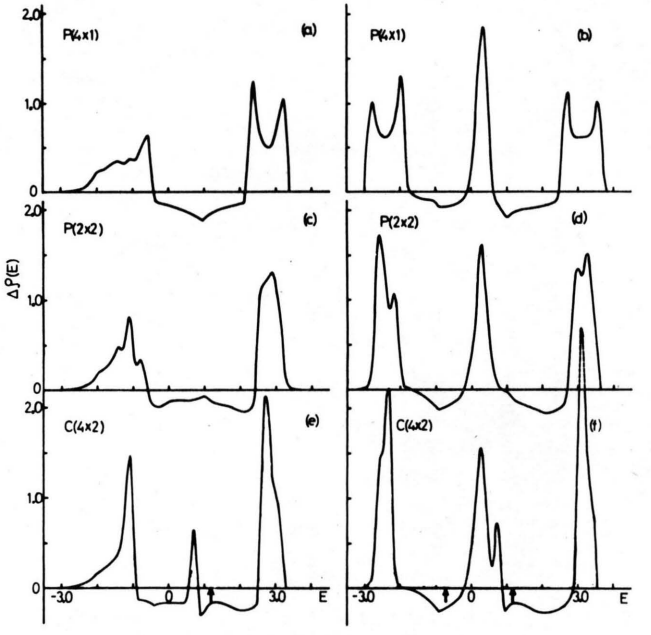

Fig. 6. The change in the electronic DOS $\Delta\varrho(E)$ during the adsorption of the $p(4\times 1)$, $p(2\times 2)$ and $c(4\times 2)$ overlayers (case B). $E_1 = 1.2$, $E_2 = -0.7$, $V_1 = 1.2$, $V_2 = 0$ (6a, 6c and 6e), and $V_2 = 1.2$ (6b, 6d and 6f) are used.

for Figs. 6a), (c) and (e), and $V_2 = 1.2$ (1.92 eV) for Figs. 6(b), (d) and (f). From these sets of parameters V_1 and V_2, it is possible to discuss the effects of having two level adsorbates on the TB metal surfaces (the left part of Fig. 6 is for the single level adsorbate). One can clearly observe in Fig. 6 that the shape and number of resonance peaks of $\Delta\varrho(E)$ curves for the two-level adsorbate are different from those for the single-level adsorbate. This indicates that the electronic states of chemisorbed layers are sensitive to the adsorbate (dissociated or undissociated) states, and can in principle be used to identify the adsorbate states as will be discussed later. Furthermore, comparing the $\Delta\varrho(E)$ curves in Figs. 5 and 6, we can state that the electronic states of ordered adsorbate (with two levels) layers depend sensitively on the adsorbate structure as well as to the adsorbate coverage.

In general, the $\Delta\varrho(E)$ curves in Figs. 5 and 6 have three prominent resonance peaks I, II and III (from lower energy to higher energy), except for the $c(2\times 2)$ overlayer: The appearance of the additional resonance peak for the $c(2\times 2)$ overlayer is due to the same reason as described in the Subsection 3.1. In order to investigate the V_2 dependence of the covalent admixture between adorbitals E_1 and E_2, we have calculated the adorbital DOS $\varrho_a(E)$. In Fig. 7, we show the adorbital DOS for the $p(2\times 1)$ overlayer with $V_2 = 0.4$ and $V_2 = 1.2$. In these figures, it can be noticed that the indirect adorbital mixing (i.e., contributions of the adorbital E_i, $i = 1$ or 2, to the resonance peaks I and II) between two strong chemisorption bonds ($V_1 = V_2 = 1.2$) is reduced relative to that between one weak and one strong ($V_1 = 1.2$, $V_2 = 0.4$) chemisorption bond. The contribution of adorbital 2 at E_2 to the resonance peak I is strongly reduced when the hopping parameter V_2 is increased from 0.4 to 1.2. Here, the resonance I is bonding on all orbitals and resonance II is anti-bonding for adorbitals E_1 and E_2.

The above mentioned V_2 dependence of covalent admixture is also seen in the other type overlayers, and in contrast to our intuitive expectation that the increase of the hopping interactions V_1 and V_2 enhances the admixture interaction between adorbitals E_1 and E_2. In the problem of the single (isolated) adsorbate chemisorption, Cunningham et al. [15] have already pointed out that the reason for this behavior is due to the competition with substrate electrons for bonding (i.e., due to strong coupling between adsorbate and substrate orbitals). One can thus see that this behavior of the adorbital mixing is common to the Case B adsorbates and not changed by the adsorbate interactions. This conclusion is not a priori obvious and can be recognized only from actual numerical calculations.

3.3. Dissociated Chemisorption

Experimental techniques such as infrared adsorption [24], energy loss spectroscopy [25] and UV photo-emission (UPS) [12, 26] have been successful in investigating the adsorbate states, i.e., in distinguishing the molecule or dissociated state of diatomic (CO, NO et.) molecules on metal surfaces. Furthermore, UPS techniques have been used to monitor the time-dependence of such dissociation process [13]. In view of this, it is quite desirable to establish a theoretical method to calculate the electronic structure of the chemisorbed layers taking into account the details of adsorbate states (molecule or dissociated states).

In this subsection, we present the simple model calculation for the dissociation of the chemisorbed species on the TB metal surfaces. If the adsorbed species (AB diatomic molecule) are dissociated, then the change in the DOS $\Delta\varrho(E)$ curve should be a linear sum of the $\Delta\varrho(E)$ curves from adsorbed A and B atomic layers both in a given surface geometry, as has been pointed out by Plummer [12]. We have calculated $\Delta\varrho(E; E_A)$ and $\Delta\varrho(E; E_B)$ and compared with the corresponding $\Delta\varrho(E; E_A, E_B)$ curve (undissociated). This comparison is shown in Fig. 8 for $c(2\times 2)$ and $c(4\times 2)$ ordered overlayers. In these calculations, we have assumed, for simplicity, that the unperturbed adsorbate levels E_1 and E_2 remain unchanged during the dissociation (though the present phase-shift technique can take account of the changes in the adsorbate level E_1 and E_2 upon the dissociation). Therefore, the difference between $\Delta\varrho(E; E_A, E_B)$ and $\Delta\varrho(E; E_A) + \Delta\varrho(E; E_B)$ curves is considered to be minimum for the present case.

In Fig. 8 one can observe tha the change in the DOS curve, $\Delta\varrho(E; E_A) + \Delta\varrho(E; E_B)$ 8c and 8d, shows rich and more complex structure (resonance, antiresonance and depletion region) than the corresponding $\Delta\varrho(E; E_1, E_2)$ curve (before dissociation) 8e and 8f; $E_A = E_1$ and $E_B = E_2$ are used. This is common to the ordered overlayers considered here and indicates that there are marked differences

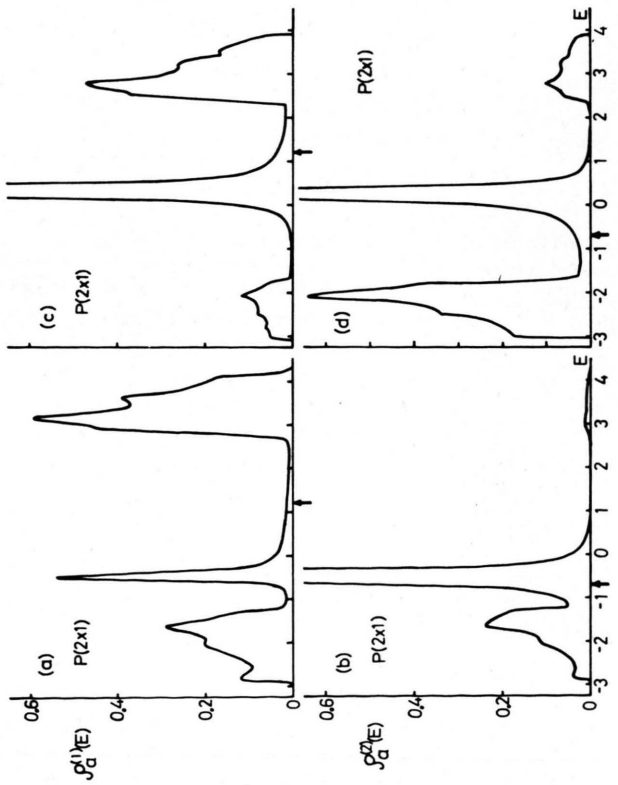

Fig. 7. Adorbital DOS $\varrho_a(E)$ for the $p(2\times1)$ overlayer (case B). $E_1 = 1.2$, $E_2 = -0.7$, $V_1 = V_2 = 1.2$ (7c and 7d), $V_1 = 1.2$ and $V_2 = 0.4$ (7a and 7b) are used.

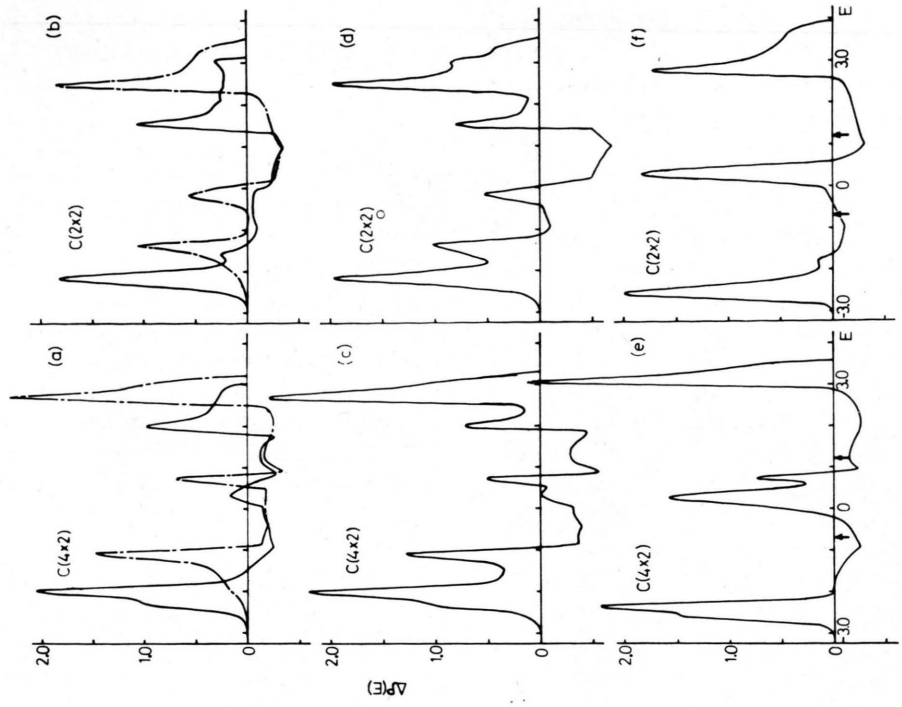

Fig. 8. Comparison between $\Delta\varrho(E; E_1, E_2)$ and $\Delta\varrho(E; E_1) + \Delta\varrho(E; E_2)$ for the $c(4\times2)$ and $c(2\times2)$ overlayers (case B). $E_1 = 1.2$, $E_2 = -0.7$ and $V_1 = V_2 = 1.2$ are used. 8(a) and 8(b) show $\Delta\varrho(E; E_i)$, $i = 1$ (dot-dashed) and $= 2$ (solid), curves: 8(c) and 8(d) do $\Delta\varrho(E; E_1) + \Delta\varrho(E; E_2)$, and 8(e) and 8(f) $\Delta\varrho(E; E_1, E_2)$.

in the $\Delta\varrho(E)$ curves between the chemisorption of the two level adsorbates and that of single level adsorbates (linear sum of each $\Delta\varrho(E)$ curve). Plummer et al. [12] have used this criterion in distinguishing the adsorbate CO (molecular or dissociated) state on transition metal surfaces.

From these findings, we come to the conclusion that the indirect interactions between two level adsorbates (Case B) play an important role in determining the electronic structure of chemisorbed overlayers. In particular, they are expected to play an essential role in the process of dissociation of di-atomic molecules on metal surfaces. These features have also been observed experimentally. Recently, Kiskinova [11] have investigated the effects of having electropositive (alkali) adatoms on the dissociation process of di-atomic colecules like CO on TM surfaces and demonstrated the importance of the adsorbate interaction on the dissociation process.

4. Conclusions

We have investigated the electronic structure of ordered adsorbate layers (with $c(2\times 2)$, $p(2\times 1)$, $p(2\times 2)$, $p(4\times 1)$ and $c(4\times 2)$ structures) on TB metal surfaces in detail, using the Green's function formalism and phase-shift technique. The adsorbate species are assumed to be located over the bridge site of the (001) surface of the model transition metal and have a π-bonding interaction with the two substrate atoms. The changes in the DOS $\Delta\varrho(E)$ and arorbital DOS have been calculated for two types of the two level adsorbates (case A and case B), and compared with those for the corresponding isolated ($\theta\approx 0$) adsorbates. For comparison, we have also investigated the chemisorption behavior of single level adsorbates.

In general, it has been shown that the indirect interactions between the two-level adsorbates play an important role in determining the electronic structure of the chemisorbed layers. Electronic states of the overlayers are very sensitive to the adsorbate coverage (θ), adsorbate structure and adsorbate species (one level or two level adsorbates). This means that the substrate (band structure) contribution is important for the chemisorption of two level adsorbates: The approximation of using a single δ-function level for the substrate is meaningless for the present problem. The present work has also shown that there are marked differences in the change in the DOS $\Delta\varrho(E)$ curves between the chemisorption of two level adsorbates and that of single level adsorbates (simulating the dissociation of diatomic molecules).

In view of the recent development of theoretical work on the chemisorption problem [27, 28], the present theory seems to be at a primitive stage. More detailed calculations from first principles are highly desirable. Nevertheless, a simple theory like the present one, exact within the one-electron approximation, is sometimes helpful in obtaining the essential features of chemisorption and also in developing a more complete theory (usually, the highly sophisticated method dealing with "real systems" does not permit the calculation of $\Delta\varrho(E)$.)

Appendix

Perturbation Matrix Elements for the π-bonding Adsorption (isolated single adsorbate $\theta\approx 0$).

In Sect. 2 we presented the explicit expressions of the $k_\parallel$ dependent adsorbate Green's functions $G_{aa}(k_\parallel; E)$ for the one-level as well as the two-level π-bonding adsorptions. These expressions can be derived from the knowledge of the perturbation (Hamiltonian) matrix elements V for the isolated single ($\theta\approx 0$) adsorbates. For a bridge site π-bonding adsorption between two substrate atoms 1 and 2 (see Fig. 1), the appropriate localized group orbital $|S_\pi\rangle$ (asymmetric under inversion along the 1—2 axis) is expressed as

$$|S_\pi\rangle = (|S_1\rangle - |S_2\rangle)/\sqrt{2}\,. \tag{A.1}$$

The perturbation matrix elements V for the π-bonding adsorption can then be given, in terms of $|S_\pi\rangle$ and adsorbate orbitals $|\alpha_i\rangle$ $i=1$ or 2, as follows: For the one-level adsorption (in terms of $|S_\pi\rangle$ and $|\alpha_1\rangle$)

$$\tilde{V}_1 = \begin{pmatrix} 0 & V_1 \\ V_1 & 0 \end{pmatrix}, \tag{A.2}$$

where we have set to zero the change in the orbital energies of the substrate and adsorbate. On the other hand, for case A and case B two-level adsorbates, they are given, in terms of $|S_\pi\rangle$, $|\alpha_1\rangle$ and $|\alpha_2\rangle$, by (A.3)

$$\tilde{V}_2^{\mathrm{A}} = \begin{pmatrix} 0 & V_1 & 0 \\ V_1 & 0 & V_c \\ 0 & V_c & 0 \end{pmatrix}, \quad \tilde{V}_2^{\mathrm{B}} = \begin{pmatrix} 0 & V_1 & V_2 \\ V_1 & 0 & 0 \\ V_2 & 0 & 0 \end{pmatrix}.$$

[1] G. A. Somorjai, Surf. Sci. **34**, 156 (1973); E. G. Derouane and A. A. Lucas, Electronic Structure and Reactivity of Metal Surfaces, Plenum Press, New York 1976.
[2] T. L. Einstein, CRC Crit. Rev. Solid State Mat. Sci. **7**, 261 (1978).
[3] S. Efrima and H. Metiv, Surf. Sci. **92**, 433 (1980).
[4] T. B. Grimley, Proc. Phys. Soc. (London) **90**, 751 (1967).
[5] T. L. Einstein and J. R. Schrieffer, Phys. Rev. **B7**, 3629 (1973).
[6] Y. Muda and T. Hanawa, Surf. Sci. **66**, 145 (1977).
[7] K. Masuda, J. de Physique **40**, 299 (1979); phys. stat. sol. **95**, 413 (1979).
[8] T. L. Einstein, Phys. Rev. **B16**, 3411 (1977).
[9] C. M. Varma and A. J. Wilson, Phys. Rev. **B22**, 3755 (1980); A. J. Wilson and C. M. Varma, Phys. Rev. **B22**, 3805 (1980).
[10] R. J. Gorte and L. D. Schmidt, Surf. Sci. **111**, 260 (1981).
[11] M. P. Kiskinova, Surf. Sci. **111**, 584 (1981).
[12] E. W. Plummer, Interactions on Metal Surfaces, Edited by R. Gomer (Topics in Appl. Phys. Vol. 4), Springer-Verlag, New York 1975, p. 143.
[13] S. Semancik and P. J. Estrup, Surf. Sci. **104**, 26 (1981).
[14] G. Doyen and G. Ertl, Surf. Sci. **43**, 197 (1974).
[15] S. L. Cunningham, M. L. Shek, and W. H. Weinberg, Appl. Surf. Sci. **4**, 127 (1980).
[16] G. Toulouse, Solid State Comm. **4**, 593 (1966).
[17] D. Kalkstein and P. Soven, Surf. Sci. **26**, 85 (1971).
[18] L. Dobrzynski and D. L. Mills, Phys. Rev. **B7**, 2367 (1973); S. L. Cunningham, W. Ho, W. H. Weinberg, and L. Dobrzynski, Appl. Surf. Sci. **1**, 33, (1977).
[19] A. Yaniv, Phys. Rev. **B22**, 4776 (1980).
[20] L. Dobrzynski, S. L. Cunningham, and W. H. Weinberg, Surf. Sci. **61**, 550 (1976); P. Masri and P. Langlade, J. Phys. **C14**, 5379 (1981).
[21] G. Allan, Ann. Phys. (Paris) **5**, 169 (1970).
[22] K. H. Lau and W. Kohn, Surf. Sci. **75**, 69 (1978).
[23] K. Masuda, Z. Naturforsch. **34a**, 600 (1979).
[24] J. T. Yates and D. A. King, Surf. Sci. **30**, 601 (1972).
[25] H. Froitzheim, H. Ibach, and S. Lehwald, Surf. Sci. **63**, 56 (1977).
[26] T. V. Vorburger, D. R. Sandstrom, and B. J. Waclawski, J. Vacuum. Sci. Tech. **13**, 287 (1976).
[27] J. P. Muscat and D. M. Newns, Prog. Surf. Sci. **9**, 1 (1978).
[28] D. W. Bullett and M. L. Cohen, Solid State Comm. **21**, 157 (1977); J. Phys. **C10**, 135 (1977).