

Electronic properties of a semi-infinite deformed linear mixed crystal

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Electronic properties of a deformed semi-infinite mixed crystal chain are studied by using the Green's-function method. The conditions for the existence of the surface states and their decay rate into the bulk are calculated in the presence of surface deformation. Calculation of the bulk properties of the semi-infinite crystal shows severe modifications due to the presence of the surface. The local densities of states in the bulk exhibit strong oscillations attributed to Bragg diffraction at the surface.

I. INTRODUCTION

Investigations of the surface properties of solids have been the subject of numerous recent investigations. The surface properties have been studied in different models using different computational techniques. One model that has been investigated quite frequently in recent years is the simple one-dimensional semi-infinite crystal. Even though most physical systems are three dimensional, the study of one-dimensional models is interesting, because the results can be obtained in closed form and the methods can usually be generalized to study three-dimensional systems. One-dimensional model calculations can then be treated as guides and testing grounds for methods before applications to more realistic systems are made. Of the various techniques available for surface studies, the Green's-function method introduced by Kalkstein and Soven¹ (KS) has been found to be quite powerful and it has been used by many authors to calculate both the surface and the bulk electronic properties of semi-infinite crystals.

In this paper, we study the electronic properties of a one-dimensional semi-infinite mixed crystal. This model system has been studied previously by Davison and others by using the scattering matrix technique^{2,3} and the molecular orbital-tight-binding approximation (MO-TBA) method.⁴⁻⁶ Although these procedures provide information regarding the existence and locations of the surface states, they are not suitable for the study of the electronic band structure on the surface layer or in the bulk. Here we reconsider this model in the Green's-function formulation of KS. This enables us to calculate not only the existence and locations of the surface states, but also their strengths and decay rates, as well as the local densities of states (LDS) of the allowed bands in the surface layer and in the bulk.

The electronic properties of an ionic crystal chain have been treated in the KS formulation by Bose and Foo⁷ in the absence of surface deforma-

tion of the resonance integral. They have shown that, for this model, there can be at the most two surface states and that the LDS show strong oscillations even deep inside the bulk. In the present paper, using the same formalism, we consider the general case where both the Coulomb integral and the resonance integral of the surface layer are modified by surface deformation. In particular, we study the effect of this surface deformation on the number of possible surface states, their strengths and decay rates as well as on the LDS of the various layers of a semi-infinite mixed *AB*-type crystal chain. This extension is quite interesting, as it allows us to interpret our results in two different ways. The modifications of the surface states and the LDS can be treated as the effects of surface deformation. On the other hand, our approach can also be regarded as a method of studying chemisorption in a crystal. In this approach, the atom at the surface layer is treated as an adatom which has been chemisorbed on the surface. From this point of view, the results can be considered as changes in the electronic properties of the system, the broadening and shift of the atomic level being due to chemisorption.

II. FORMALISM

We consider a semi-infinite mixed crystal chain consisting of two kinds of atoms *A* and *B*, as shown schematically in Fig. 1. The Coulomb integrals of these atoms are represented by ϵ_a and ϵ_b , respectively. We assume that an electron can exchange energy with its nearest neighbors only and the resonance integral between the nearest neighbors is β . As in KS, we consider that the semi-infinite crystal is formed by starting with an infinite crystal and then passing an imaginary cleavage plane between site number 0 and site number -1. Thus, the resonance integral coupling the two sides of the cleaved crystal is set equal to zero. We also consider that the surface atom undergoes deformation, so that its Coulomb and

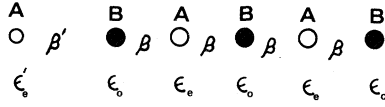


FIG. 1. Semi-infinite one-dimensional chain of a mixed crystal showing the A and B atoms.

resonance integrals assume values ϵ'_e and β' , respectively, which can be different from those of the bulk atoms. Our aim here is to calculate the changes in the surface states and the LDS of a semi-infinite crystal due to this surface deformation.

We use tight-binding approximation to describe the electronic properties of the crystal. Thus, the Hamiltonian of the cleaved mixed crystal can be written as

$$H = \epsilon'_e |0\rangle \langle 0| + \beta' |0\rangle \langle 1| + \sum_{n=1, \text{odd}}^{\infty} \epsilon_o |n\rangle \langle n| + \sum_{n=2, \text{even}}^{\infty} \epsilon_e |n\rangle \langle n| + \sum_{n=1}^{\infty} \beta |n\rangle \langle n+1|. \quad (1)$$

The Hamiltonian of the infinite mixed crystal is given by

$$\bar{H} = \sum_{n=-\infty, \text{odd}}^{\infty} \epsilon_o |n\rangle \langle n| + \sum_{n=-\infty, \text{even}}^{\infty} \epsilon_e |n\rangle \langle n| + \sum_{n=-\infty}^{\infty} \beta |n\rangle \langle n+1|. \quad (2)$$

The difference between the Hamiltonians of the cleaved crystal and the infinite perfect crystal can be treated as the scattering potential in the evaluation of the Green's function of the system. Thus, the scattering potential is

$$V = H - \bar{H}. \quad (3)$$

The Green's function for the cleaved crystal, G , can be expressed in terms of the Green's function for the perfect infinite crystal, \bar{G} , and the scattering potential V , by using the Dyson equation

$$G = \bar{G} + \bar{G}VG, \quad (4)$$

where G and \bar{G} satisfy the equations of the form

$$G = (E - H)^{-1} \quad (5)$$

and

$$\bar{G} = (E - \bar{H})^{-1}, \quad (6)$$

where H , \bar{H} , and V are defined by Eqs. (1), (2), and (3), respectively.

In the present localized representation, the operator equation (4) can be expressed as a set of algebraic difference equations,

$$G(m, m') = \bar{G}(m, m') + \sum_{l, l'} G(m, l)V(l, l')G(l', m') \quad \text{for } m, m' \geq 0, \quad (7)$$

where m, m' , etc., represent the various lattice sites. Referring to Eqs. (1), (2), and (3), we note that the only nonzero matrix elements of the scattering potential V are

$$\begin{aligned} V(-1) &\equiv V(0, -1) = V(-1, 0) = -\bar{H}(0, -1) = -\beta, \\ V(0) &\equiv V(0, 0) = H(0, 0) - \bar{H}(0, 0) = \epsilon'_e - \epsilon_e, \\ V(1) &\equiv V(0, 1) = V(1, 0) = H(0, 1) - \bar{H}(0, 1) = \beta' - \beta. \end{aligned} \quad (8)$$

Using Eq. (8) in Eq. (7) we can solve for the diagonal elements of the Green's function and obtain

$$G(m, m) = \bar{G}(m, m) + \Sigma/\Delta, \quad (9)$$

where

$$\begin{aligned} \Sigma &= [\bar{G}(m, -1)V(-1) + \bar{G}(m, 0)V(0) \\ &\quad + 2\bar{G}(m, 1)V(1)]\bar{G}(m, 0) \\ &\quad + [\bar{G}(0, 0)\bar{G}(m, 1) - \bar{G}(0, 1)\bar{G}(m, 0)]\bar{G}(m, 1)V^2(1) \end{aligned}$$

and

$$\begin{aligned} \Delta &= 1 - \bar{G}_{ee}(0, 0)V(0) - \bar{G}_{eo}(0, 1)[V(-1) + 2V(1)] \\ &\quad + V^2(1)[\bar{G}_{eo}^2(0, 1) - \bar{G}_{ee}(0, 0)\bar{G}_{oo}(1, 1)] \\ &\quad + V(1)V(-1)[\bar{G}_{eo}^2(0, 1) - \bar{G}_{oo}(1, -1)\bar{G}_{ee}(0, 0)]. \end{aligned} \quad (10)$$

Here the subscripts ee , eo , etc., are introduced explicitly to refer to the matrix elements of \bar{G} between two even sites, and between even and odd sites, respectively.

The local densities of states at each site of the mixed crystal can then be obtained by using the well-known relation

$$\rho_m(E) = -\frac{1}{\pi} \text{Im}G(m, m). \quad (11)$$

Also, since the energies of the surface states are determined by the poles of the Green's function, one observes from Eq. (9) that the surface-state energies are obtained by setting

$$\Delta = 0. \quad (12)$$

Thus, referring to Eqs. (10) and (11), we note that the local densities of states $\rho_m(E)$ and the surface-state energies have been expressed in terms of the various matrix elements of the Green's function of the perfect infinite mixed crystal and the scattering potential V . The matrix elements of the Green's function can be easily calculated and we now present some of those that become useful in subsequent evaluations.

(1) Even lattice sites, i.e., m and n are even.

(i) Diagonal elements:

$$\bar{G}_{ee}(m, m) = \bar{G}_{ee}(0, 0) = \frac{E - \epsilon_o}{(A^2 - B^2)^{1/2}},$$

where

$$A = (E - \epsilon_e)(E - \epsilon_o) - 2\beta^2 \text{ and } B = 2\beta^2.$$

(ii) Off-diagonal elements between even sites:

$$\bar{G}_{ee}(m, n) = \bar{G}_{ee}(0, 0)z^{1/2|m-n|}$$

with

$$z = \frac{1}{2}[\alpha - (\alpha^2 - 4)^{1/2}] \text{ and } \alpha = 2A/B.$$

(2) Odd lattice sites, i.e., m and n odd.

(i) Diagonal elements:

$$\bar{G}_{oo}(m, m) = \frac{E - \epsilon_e}{E - \epsilon_o} \bar{G}_{ee}(0, 0) = \bar{G}_{oo}(1, 1). \quad (13)$$

(ii) Off-diagonal elements between odd sites:

$$\begin{aligned} \bar{G}_{oo}(n, m) &= \bar{G}_{oo}(m, n) = \frac{E - \epsilon_e}{E - \epsilon_o} \bar{G}_{ee}(0, 0)z^{1/2|m-n|} \\ &= \frac{E - \epsilon_e}{E - \epsilon_o} \bar{G}_{ee}(m+1, n+1). \end{aligned}$$

(3) Elements between even and odd sites:

$$\begin{aligned} \bar{G}_{oe}(m, 0) &= \bar{G}_{eo}(0, m) \\ &= \frac{\beta}{E - \epsilon_o} [\bar{G}_{ee}(m-1, 0) + \bar{G}_{ee}(m+1, 0)], \end{aligned}$$

$$\begin{aligned} \bar{G}_{oe}(n, m) &= \bar{G}_{eo}(m, n) \\ &= \frac{\beta}{E - \epsilon_o} [\bar{G}_{ee}(m-n-1, 0) \\ &\quad + \bar{G}_{ee}(m-n+1, 0)] \\ &\quad \text{if } m-n+1 > 0, \end{aligned}$$

$$\begin{aligned} \bar{G}_{oe}(n, m) &= \bar{G}_{eo}(n, m) \\ &= \frac{\beta}{E - \epsilon_o} [\bar{G}_{ee}(n-m+1, 0) \\ &\quad + \bar{G}_{ee}(n-m+3, 0)] \\ &\quad \text{if } m-n-1 < 0. \end{aligned}$$

These expressions for the matrix elements of the Green's function \bar{G} are used in Eqs. (11) and (12)

$$L^2 = \frac{[\bar{G}(2, -1)V(-1) + \bar{G}(2, 0)V(0) + 2\bar{G}(2, 1)V(1)]\bar{G}(2, 0) + [\bar{G}(0, 0)\bar{G}(2, 1) - \bar{G}(0, 1)\bar{G}(2, 0)]\bar{G}(2, 1)V^2(1)}{[\bar{G}(0, 1)V(-1) + \bar{G}(0, 0)V(0) + 2\bar{G}(0, 1)V(1)]\bar{G}(0, 0)}. \quad (16)$$

Again, using Eq. (13) in Eq. (16), we find

$$L^2 = z^2 + \frac{\beta V(1)(1-z^2)[2z + \bar{G}(2, 1)V(1)]}{(E - \epsilon_o)V(0) + \beta(1+z)[V(-1) + 2V(1)]} \Big|_{E=E_s}, \quad (17)$$

where z has been defined in Eq. (13). The condition for the existence of a surface state is that

$$0 < L^2 < 1. \quad (18)$$

to calculate the LDS and the energies of the surface states.

Surface states. Substituting Eq. (13) in Eq. (10) and using Eq. (12), we obtain the following third-order polynomial equation for the energy of the surface states of the semi-infinite mixed crystal:

$$(1 - \gamma^2)E_e^3 + [(1 - \gamma^2)\Delta + (2 - \gamma^2)\Delta']E_e^2 + [(2 - \gamma^2)\Delta\Delta' + \Delta'^2 + \gamma^2\beta'^2]E_e + \Delta'^2\Delta = 0, \quad (14a)$$

where $E_e = E - \epsilon_e$, $\Delta = \epsilon_e - \epsilon_o$, $\Delta' = \epsilon_e - \epsilon'_e$, and $\gamma = \beta'/\beta$. If we measure all energies with respect to β , i.e., if we set $\beta = 1$, Eq. (14a) takes the following dimensionless form:

$$(1 - \beta'^2)E_e^3 + [(1 - \beta'^2)(\Delta + \Delta') + \Delta']E_e^2 + [(1 - \beta'^2)\Delta\Delta' + \Delta'(\Delta + \Delta') + \beta'^4]E_e + \Delta\Delta'^2 = 0. \quad (14b)$$

It can be easily checked that, in the absence of the surface deformation of the resonance integral, i.e., for $\beta' = \beta$, Eq. (14a) reduces to Eq. (13) of Ref. 7. This confirms the fact that the surface states of the ionic crystals and the mixed crystals have the identical energies, even though the wave functions have a phase shift.⁸ Equations (14a) and (14b) indicate that, in the presence of surface deformation, three different surface states may exist in a mixed crystal, whereas in the absence of surface deformation there may be at the most two surface states.⁷ However, all three surface states may not exist simultaneously as the existence of the surface states is determined by the relative values of ϵ_e , ϵ_o , β' , and ϵ'_e . Information regarding the existence of the surface states may be obtained by using the physical requirement that the wave function of a true surface state must decay exponentially into the bulk.^{7,8} The decay constant L of a surface state is given by

$$L^2 = \frac{\rho_{m+2}}{\rho_m} \Big|_{E=E_s}, \quad (15)$$

where E_s is a solution of Eq. (14a). Using Eqs. (9) and (11) in Eq. (15), we obtain

III. RESULTS AND DISCUSSIONS

In Fig. 2, we have plotted the local densities of states (LDS) in the allowed energy bands for the first four layers ($m = 0$ to 3) for $\epsilon_e = -\epsilon_o = 1$, $\beta' = 1$, and $\epsilon'_e = \epsilon_e$. Note that this corresponds to the case of undeformed surface. The dashed curves in this diagram depict the densities of states

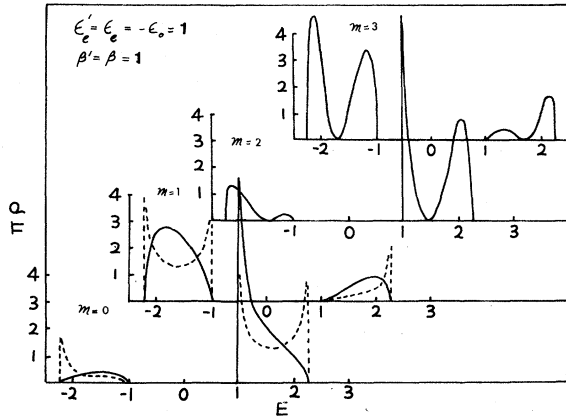


FIG. 2. Local density of states for the surface ($m=0$) and first three interior ($m=1$ to 3) layers for the undeformed surface ($\epsilon_e = -\epsilon_o = 1$, $\beta' = \beta = 1$, and $\epsilon'_e = \epsilon_e$). For this case no surface states appear.

of the perfect infinite mixed crystal, which are presented here to facilitate comparison. We find that, in this case, the existence condition [Eq. (18)] for the surface state is not satisfied by any of the solutions of Eq. (14), which implies that the undeformed surface does not introduce any surface states outside the allowed energy bands. The presence of the surface, however, drastically modifies the LDS at various layers as these LDS

do not have much resemblance with those of the perfect crystal. The band-edge singularities of the perfect crystal are smoothed out and at the interior layers the LDS show strong oscillations. In fact, this oscillatory behavior persists in the deep bulk layers, even though the envelopes of these oscillations resemble the LDS of the perfect crystal. Such oscillations in one-dimensional systems have been reported by other authors^{9,10} and have been discussed in detail by Bose and Foo.⁷ These oscillations have been attributed to an interference effect due to surface scattering. It has been shown that certain local pseudoenergy gaps would appear at those values of E at which Bragg-like diffraction conditions are satisfied. An average of these oscillatory LDS over a certain number of bulk layers, however, reproduces the densities of states of the perfect infinite crystal.

The energies of the allowed surface states for other values of ϵ'_e and β' can be calculated by using Eqs. (14) and (18). In order to visualize the evolution of the surface states and the corresponding changes in the LDS as function of ϵ'_e and β' , we have plotted in Fig. 3, the surface states (as depicted by the arrows) and the LDS of the surface layer ($m=0$) for three values of ϵ'_e (-0.5 , 0 , 0.5) and six values of β' (0.4 , 0.6 , 1.0 , 1.4 , 1.8 , 2.0). It is interesting to note that for small values of β' (< 1) only one surface state appears inside

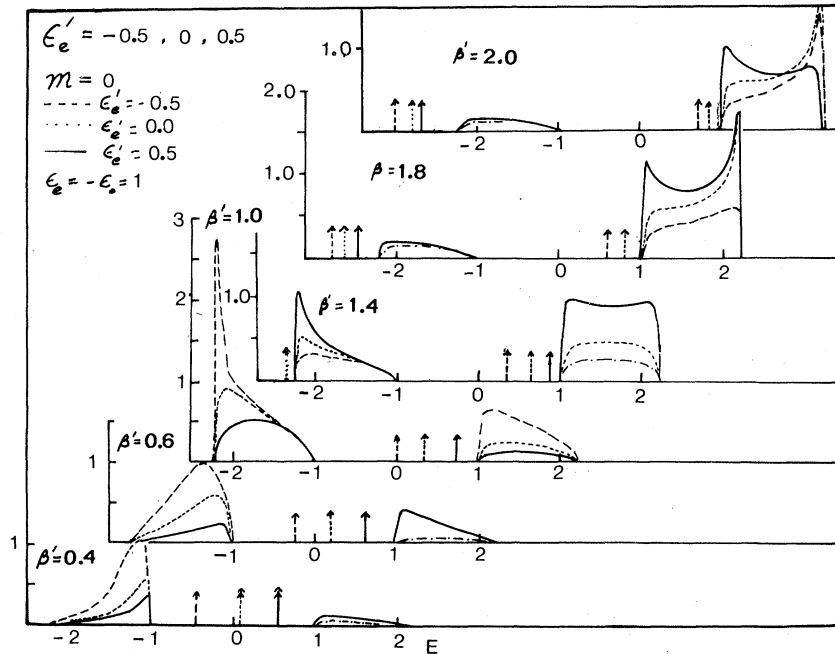


FIG. 3. Local density of states for the surface ($m=0$) layer for three values of ϵ'_e and six values of β' as shown. The dashed, dotted, and solid curves for each value of β' correspond to the cases for $\epsilon'_e = -0.5$, 0 , and 0.5 , respectively. Surface states appear in the gap or below the lower band, the positions of which are shown by the corresponding (solid, dotted, or dashed) arrow.

the band gap for each value of ϵ'_e . However, for $\beta' > 1$, surface states may appear not only inside the band gap but also below the lower band (as shown) and above the upper band. We have also found that for $\epsilon'_e > 1$ as β' increases, the surface states inside the band gap disappear while two surface states appear, one below the lower band and another above the upper band. Note that in each case in this figure, the local densities of states are also affected by ϵ'_e and β' . Since β' corresponds to the strength of interaction of the surface atom with the rest of the crystal, for small values of $\beta' (< 1)$, the surface atom behaves like an individual unattached atom weakly bound to the crystal. Consequently, for these values of β' , the surface state appears near the atomic level ϵ'_e (only slightly modified by β') for each value of ϵ'_e . This is also the reason that the surface state has higher strength and the electronic densities of states in the energy bands are weaker. However, as β' increases, there is stronger interaction of the surface atom with the rest of the crystal and the surface atom loses its individual character. Thus, for larger values of β' , the surface states move away from ϵ'_e , their strength is reduced, and the band densities of states increase in strength.

The decay of the allowed surface states into the bulk is governed by Eq. (18). To demonstrate how a surface state decays, we have plotted in Fig. 4

the surface state and the LDS for the surface layer ($m = 0$) and the first four interior layers ($m = 1$ to 4) for the case of $\epsilon'_e = 0.5$ and $\beta' = 1.2$. The dashed curves again represent the densities of states of the perfect infinite crystal. For this case, Eq. (14) produces a single surface state at $E \approx 0.83$ (shown by the arrow). Its strength (represented by the height of the arrow) at the surface layer is determined by the well-known sum rule satisfied by the LDS for each layer, viz.,

$$\rho_{\text{surface}} = 1 - \int_{\text{band}} \rho(E) dE, \quad (19)$$

where the integral is carried out over the LDS of the allowed energy bands. The decay rate of this surface state is calculated by using Eq. (18) and, as expected, the surface state decays exponentially into the bulk layers. The LDS in the bulk layers gain in strength and show oscillations. However, the number of these oscillations are not affected by the values of β' and ϵ'_e (cf. Fig. 2).

Under proper conditions, the surface atom can introduce a resonancelike behavior in the LDS of the surface layer, as shown in Fig. 5, where we have plotted the LDS for the first five layers ($m = 0$ to 4) for $\epsilon'_e = 1.5$ and $\beta' = 0.4, 1.0, \text{ and } 1.4$. In the case of $\beta' = 0.4$, there is a very large peak in the LDS of the upper band of the surface layer ($m = 0$) at $E \approx 1.55$, which is expected, because the

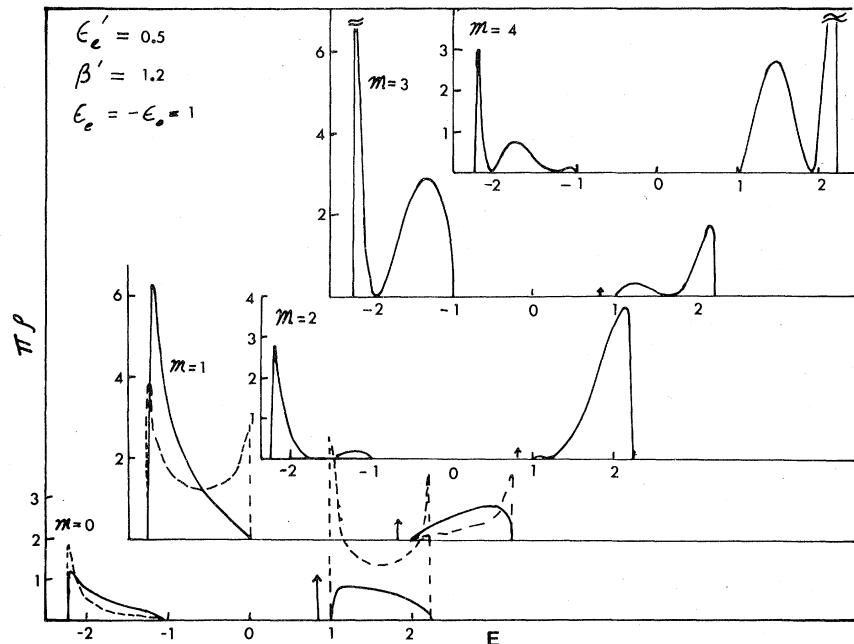


FIG. 4. Local density of states for the surface and first four interior layers ($m = 0$ to 4) for $\epsilon'_e = 0.5$ and $\beta' = 1.2$. The locations and strengths of the surface states are given by the positions and the heights of the arrows in the gap. The scale of the surface state is 2 times that of the bulk density of states.

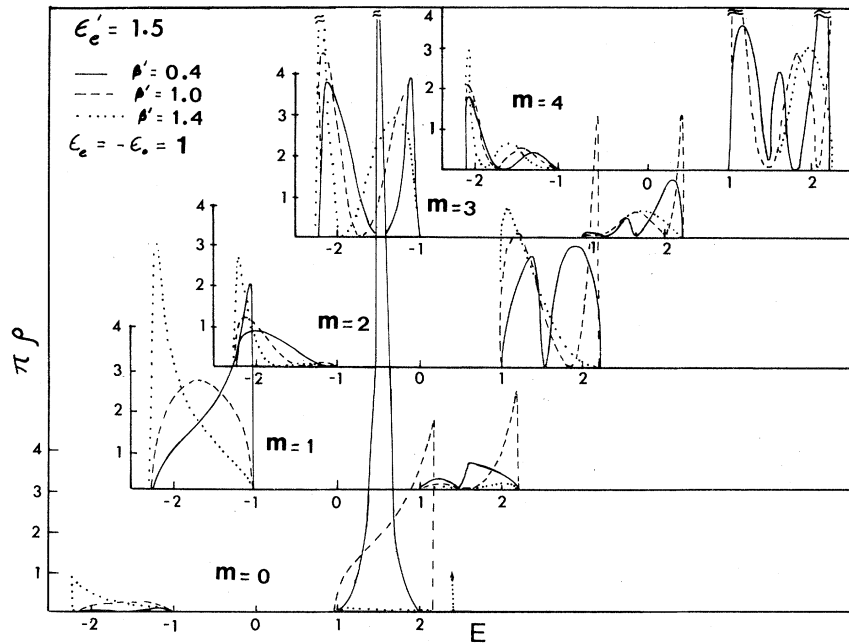


FIG. 5. Local density of states for the surface and first four interior layers ($m=0$ to 4) for $\epsilon'_e=1.5$ and $\beta'=0.4$, 1.0, and 1.4, respectively. A surface state appears for $\beta'=1.4$ above the upper band. The large peak in the LDS of the upper band of the surface layer for $\beta'=0.4$ corresponds to a resonance between the discrete level of the adatom and the continuum states of the upper band.

value of the surface Coulomb integral $\epsilon'_e (= 1.5)$ lies inside the upper band and the value of the surface resonance integral $\beta' (= 0.4)$ is relatively small, so that the atomic character of the surface atom is largely retained. In the language of the chemisorption, it may be stated that this peak appears due to a resonance between the discrete level of the adatom and the continuum states of the upper band. Because of the interaction via β' , the center of the peak is slightly shifted to a higher value. For larger values of β' , the surface atom loses its atomic character and no such resonance is observed. For $\beta' = 1$, the existence of the surface states is precluded by Eq. (18), and a relatively large peak is observed at the band edge. For $\beta' = 1.4$, this peak is shifted even further and a surface state appears at $E \approx 2.36$ (shown by dotted arrow). As we penetrate deeper into the bulk, the LDS show strong oscillations in all three cases, as expected. The surface state for $\beta' = 1.4$ persists in the bulk layers (not shown), even though its strength is reduced by a factor of L calculated in Eq. (18).

IV. SUMMARY

The surface properties of a one-dimensional semi-infinite mixed crystal have been studied by the Green's-function method of KS, which enabled us to investigate the behavior of the surface states and the local densities of states in the presence of surface deformation. We have shown that there can be at the most three surface states for this system. The locations and strengths of these surface states are determined by the Coulomb integral ϵ'_e and the resonance integral β' of the surface atom. We have found that, depending on the values of these parameters, there may be zero, one, two, or three allowed surface states. As expected, the allowed surface states are found to decay exponentially into the bulk. The local densities of states are drastically modified in the presence of the deformed surface. The usual Van Hove singularities at the edges are smoothed out and the LDS develop oscillations in the bulk layers.

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