PHYSICAL REVIEW B VOLUME 10, NUMBER 8 15 OCTOBER 1974

Electronic properties of a semi-infinite ionic crystal chain

Shyamalendu M. Bose and E-Ni Foo
Department of Physics and Atmospheric Science, Drexel University, Philadelphia, Pennsylvania 19104

(Received 14 March 1974)

Electronic properties of a semi-infinite linear chain of an ionic crystal, simulated by assigning s and p orbitals on alternate sites, have been studied by using the Green's-function method. We obtain the same results for the energy and the decay constant of the surface states as those obtained by using the linear-combination-of-atomic-orbitals (LCAO) method. The Green's-function method also allows us to study the properties of the bulk states which show severe modifications owing to the presence of the surface. In particular, we show that the bulk local densities of states develop strong oscillatory behavior and that there exist certain Bragg-like conditions at which both the real and the imaginary part of the local Green's function go to zero.

I. INTRODUCTION

The existence of a surface in a solid leads to various important and interesting modifications of its properties. The surface states and their properties have been studied by many authors by various methods. Historically, Tamm[1] first used the Kronig-Penney model to study the surface states of a one-dimensional crystal and showed that under certain conditions surface states might exist. Goodwin[2] was the first to apply the linear-combination-of-atomic-orbitals (LCAO) model to study the Tamm states of a crystal. In this model the Coulomb integrals and the resonance integrals of the surface atoms are taken to be different from those in the bulk. This method was further generalized by Koutecky[3] and Koutecky and Tomasek[4] to study the energy and existence conditions of surface states.

Recently Kalkstein and Soven (KS)[5] introduced a Green's-function formalism to study the surface states of a semi-infinite crystal. This turns out to be a very powerful method by which both the surface and bulk properties of a semi-infinite crystal[6,7] can be studied to obtain exact results. In this paper we have studied the electronic properties of a semi-infinite one-dimensional ionic crystal by this Green's-function method. The study of such a simple one-dimensional model would enable us to draw certain general conclusions regarding the surface properties of a three-dimensional ionic crystal such as NaCl and CdS (in general known as MX ionic crystals). Since the surfaces of ionic crystals are usually natural crystal surfaces and have almost no surface reconstruction, it is very simple and convenient to apply the Green's-function method to such a system. Surface states of such an ionic crystal have been studied by several authors[8-10] by different methods. Recently Levine and Davison (LD)[10] have made a detailed study of the surface states of a one-dimensional ionic crystal using a band-edge LCAO method. By this method they were able to show that under certain existence conditions a M-like (X-like) surface state would appear in the energy band gap somewhat below (above) the conduction (valence) band when the chain is terminated by an M-like (X-like) atom. In this paper, we first show that, for this model, the Green's-function method produces exactly the same results for both the energy and the decay constant of the surface state. By this method we have also been able to calculate the densities of the bulk states which show severe modifications. The bulk densities of states develop oscillatory structures and the band edges get modified due to the presence of the surface.

In Sec. II we discuss the Green's-function formalism for an ionic crystal and present our results. In Sec. III we briefly discuss the main conclusions of our work.

II. FORMALISM

Following LD we assume that in an ionic crystal the resonance integrals β created by the s orbital on the M sites and the p orbitals on the X sites have alternate signs along a chain. As shown in Fig. 1, we thus consider a one-dimensional representation of a semi-infinite ionic crystal of the MX-type where we assume that the M-like states are located in the even-numbered sites and the X-like states in the odd-numbered sites. For the purpose of our calculation, we also suppose that the crystal is terminated at the zeroth site where the Coulomb integral ϵ_e' is different from the Coulomb integrals ϵ_e on the other even sites inside the bulk. We represent the Coulomb integrals on the X sites by ϵ_o. Following KS we assume this this crystal is formed by starting with an infinite perfect crystal and then passing an imaginary cleavage plane between site number 0 and site number -1. Thus the resonance integral β which couple the two sides of the cleaved crystal is set to be zero and the difference between the Hamiltonians of the cleaved crystal and that of

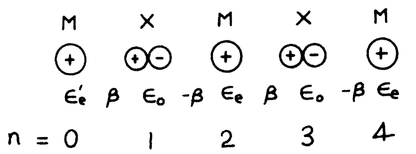

FIG. 1. Semi-infinite one-dimensional chain of an ionic crystal showing the M-like and X-like atoms. The symmetry types of the orbital wave functions, Coulomb and resonance integrals are also shown.

the perfect crystal is treated as the scattering potential. The Green's function for the cleaved crystal is expressed in terms of the Green's function for the infinite perfect crystal and the scattering potential by a Dyson equation

$$G=\bar{G}+\bar{G}VG, \tag{1}$$

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

$$(E-H)G=1, \quad (E-\bar{H})\bar{G}=1, \tag{2}$$

where H and $\bar{H}$ are the Hamiltonians for the cleaved and perfect crystals. The perturbation potential V in Eq. (1) is given by $V=H-\bar{H}$.

In our present model the matrix elements of $\bar{H}$ between localized functions centered on different sites are

$$\begin{aligned}\bar{H}_{mm}&=\epsilon_e, \quad m \text{ even}\\ &=\epsilon_0, \quad m \text{ odd};\end{aligned} \tag{3}$$

these are the so-called Coulomb integrals we have referred to before. Like LD we assume $\epsilon_e > \epsilon_0$. Also the resonance integrals between the nearest neighbors in our model are

$$\begin{aligned}\bar{H}_{m,m+1}=-\bar{H}_{m,m-1}&=\beta, \quad m \text{ even}\\ &=-\beta, \quad m \text{ odd}.\end{aligned} \tag{4}$$

We ignore all other resonance integrals, i.e., we retain only the nearest-neighbor interactions in our calculation.

Let us now write down the various matrix elements of the scattering potential V. Since the Hamiltonian of the cleaved crystal cannot have any matrix elements between localized functions centered on different sides of the cleavage plane, we must have

$$H(0,\,-1)=0,$$

otherwise

$$H(m,\,m+1)=-H(m,\,m-1)=\bar{H}(m,\,m+1).$$

Also as noted before the Coulomb integral of the M atom at the surface is $H(0,0)=\epsilon_e'$ otherwise

$$H(m,\,m)=\bar{H}(m,\,m) \quad \text{for } m>0.$$

Thus the various nonzero matrix elements of the perturbation potential are

$$\begin{aligned}&V(0,\,-1)=-\bar{H}(0,\,-1)=-\beta,\\ &V(-1,\,0)=-\bar{H}(-1,\,0)=-\beta,\\ &V(0,\,0)=H(0,\,0)-\bar{H}(0,\,0)=\epsilon_e'-\epsilon_e.\end{aligned} \tag{5}$$

In the present localized representation, the operator equation (1) can be expressed as a set of algebraic difference equations,

$$\begin{aligned}G(m,\,m')=\bar{G}(m,\,m')+\sum_{l,l'}\bar{G}(m,\,l)V(l,\,l')\\ \times G(l',\,m').\end{aligned} \tag{6}$$

Remembering that the only nonzero matrix elements of V are given by Eq. (5) and that $G(m,\,m')=0$ if m and m' refer to sites on opposite sides of the cleaved crystal, we have from Eq. (6),

$$\begin{aligned}G(m,\,m)&=\bar{G}(m,\,m)\\ &+\frac{[\bar{G}(m,\,0)V(0,\,0)+\bar{G}(m,\,-1)V(-1,\,0)]\bar{G}(0,\,m)}{1-\bar{G}(0,\,0)V(0,\,0)-\bar{G}(0,\,-1)V(-1,\,0)}.\end{aligned} \tag{7}$$

The local density of states (LDS) at the site m will be given by

$$\rho_m(E)=-\frac{1}{\pi}\operatorname{Im}[G(m,\,m)]. \tag{8}$$

Also the energies of any possible surface state can be determined from the zeros of the denominator of Eq. (7), i.e., the surface-state energy is given by the solution of

$$1-\bar{G}_{ee}(0,\,0)V(0,\,0)-\bar{G}_{eo}(0,\,-1)V(-1,\,0)=0 \tag{9}$$

In Eq. (9), the subscripts ee and eo refer to the matrix elements of $\bar{G}$ between two even sites and between one even and one odd site, respectively. The various matrix elements of the perfect Green's function $\bar{G}$ in our model are found to be

$$\begin{aligned}&\bar{G}_{ee}(m,\,m)=\frac{1}{E-\epsilon_e}\left(1-\frac{4\beta^2}{(E-\epsilon_e)(E-\epsilon_0)}\right)^{-1/2},\\ &\qquad m \text{ even}\\ &\bar{G}_{oo}(m,\,m)=\frac{E-\epsilon_e}{E-\epsilon_0}\bar{G}_{ee}(0,\,0),\\ &\qquad m \text{ odd}\\ &\bar{G}_{ee}(m,\,0)=\bar{G}_{ee}(0,\,m)=\bar{G}_{ee}(0,\,0)\\ &\qquad\times\{\tfrac{1}{2}[\alpha-(\alpha^2-4)]^{1/2}\}^{m/2}, \quad m \text{ even}\\ &\bar{G}_{eo}(m,\,-1)=\frac{\beta}{E-\epsilon_0}[\bar{G}_{ee}(0,\,m)-\bar{G}_{ee}(0,\,m+2)],\\ &\qquad m \text{ even}\\ &\bar{G}_{oe}(m,\,0)=\bar{G}_{eo}(0,\,m)=\frac{\beta}{E-\epsilon_0}[\bar{G}_{ee}(0,\,m+1)\end{aligned} \tag{10}$$

$$-\overline{G}_{ee}(0,\ m-1)]\ ,\quad m \text{ odd}$$

$$\overline{G}_{oo}(m,\ -1)=\frac{E-\epsilon_e}{E-\epsilon_o}\,\overline{G}_{ee}(0,\ m+1),\quad m\text{ odd}$$

where

$$\alpha=2-\frac{(E-\epsilon_o)(E-\epsilon_e)}{\beta^2}\ . \tag{11}$$

Expressing $\overline{G}_{oe}(0,\ -1)$ in terms of $\overline{G}_{ee}(0,\ 0)$ from Eq. (10) we find that Eq. (9) reduces to

$$\overline{G}_{ee}(0,\ 0)(2\epsilon_e'-\epsilon_e-E)=1\ ; \tag{12}$$

substituting for $\overline{G}_{ee}(0,\ 0)$ from Eq. (10), Eq. (12) becomes

$$(E-\epsilon_o)(E-\epsilon_e')(\epsilon_e'-\epsilon_e)-\beta^2(E-\epsilon_e)=0\ . \tag{13}$$

The solution of this equation for E then defines the energy of the surface states for a semi-infinite ionic crystal terminated by an M-like atom at the surface. This is exactly the result obtained by LD [cf. Eq. (34d) of Ref. 10].

Notice that in order that the surface state may lie in the band gap, i.e., in the region $\epsilon_o < E < \epsilon_e$ we must have from Eq. (13)

$$(E-\epsilon_e')(\epsilon_e'-\epsilon_e)<0\ , \tag{14}$$

which implies that the surface state will lie in the band gap if $\epsilon_e' < E < \epsilon_e$. The position of this surface state in the band gap has been graphically analyzed by LD.

We expect that the wave function corresponding to the surface state would decay exponentially into the bulk. Let us then proceed to calculate the decay constant of the surface state corresponding to the crystal terminated by an M-like atom. Such a decay constant L is given by

$$L^2=\frac{\rho_{m+2}\ (E_{\text{surface}})}{\rho_m\ (E_{\text{surface}})}\ . \tag{15}$$

As indicated in Eq. (15), this ratio must be calculated for the surface state only, i.e., for energy E equal to the surface energy. Using Eqs. (7) and (8) in Eq. (15), we obtain

$$L^2=\left.\frac{[\overline{G}(m+2,\ 0)V(0,\ 0)+\overline{G}(m+2,\ -1)V(-1,\ 0)]\overline{G}(0,\ m+2)}{[\overline{G}(m,\ 0)V(0,\ 0)+\overline{G}(m,\ -1)V(-1,\ 0)]\overline{G}(0,\ m)}\right|_{E=E_{\text{surface}}}\ . \tag{16}$$

Again using Eq. (10) in Eq. (16), we get

$$L^2=\left(\frac{\overline{G}(0,\ m+2)}{\overline{G}(0,\ m)}\right)^2=\left(\frac{\overline{G}(0,\ 2)}{\overline{G}(0,\ 0)}\right)^2_{E=E_{\text{surface}}}\ . \tag{17}$$

Thus the decay constant of an M-like surface state, using Eq. (10) in Eq. (17), becomes

$$L=\frac{\overline{G}(0,\ 2)}{\overline{G}(0,\ 0)}=\tfrac{1}{2}[\alpha-(\alpha^2-4)^{1/2}]_{E=E_{\text{surface}}}\ . \tag{18}$$

Substituting for $\overline{G}(0,\ 0)$ in Eq. (18) from Eq. (12), we obtain

$$L=\frac{E-\epsilon_e'}{\epsilon_e-\epsilon_e'}\ . \tag{19}$$

This is exactly what was obtained by LD [cf. Eq. (34a) of Ref. 10] for the decay constant of an M-like surface state.

To study the nature of the decay of the surface state and the modifications of the bulk states owing to the presence of the surface we have calculated numerically the local density of states (LDS) via Eqs. (7) and (8). The results of our calculation for $\epsilon_e=-\epsilon_o=1$, $\beta=1$, and $\epsilon_e=0.5$ for the surface layer and the first three interior layers are shown by A, B, C, D, respectively, of Fig. 2. The dashed curves in this figure are the LDS of an infinite perfect crystal. Notice that the surface state occurring at $E\approx 0.76$ decay exponentially (denoted by the height of arrows representing the surface state at each layer) within each sublattice. However, because of the presence of the two sublattices, it appears that the surface state decays in an oscillatory fashion. It is also interesting to note that the LDS at the surface layer does not have much resemblance with the LDS for the pure crystal. The band-edge singularities of the infinite pure crystal

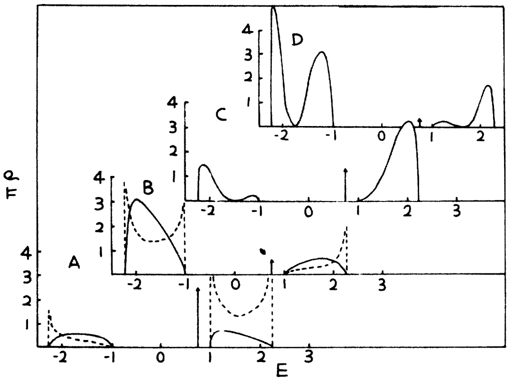

FIG. 2. Local density of states for the surface ($m=0$) and first three interior layers for $\epsilon_e=-\epsilon_o=1$, $\beta=1$, and $\epsilon_e'=0.5\ \epsilon_e$. The dashed curves in A and B are the infinite crystal density of states at an M and X layer, respectively. Surface state occurring at $E\approx 0.76$ is shown by an arrow.

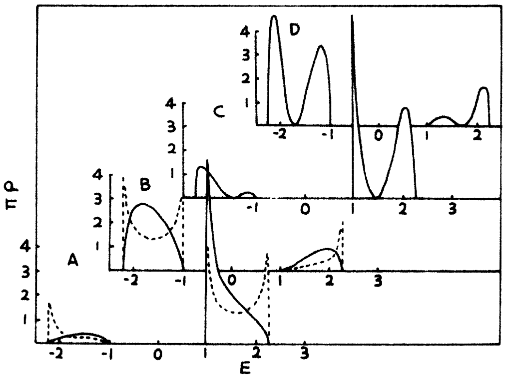

FIG. 3. Local density of states for the surface ($m = 0$) and first three interior layers for $\epsilon_e = -\epsilon_0 = 1$, $\beta = 1$, and $\epsilon_e' = \epsilon_e$. Notice no surface state appears in the gap.

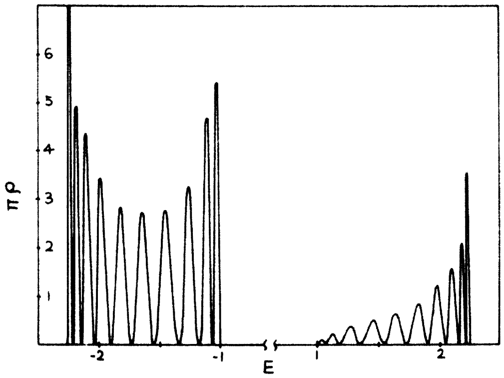

FIG. 5. Local density of states for the 19th layer for $\epsilon_e = -\epsilon_0 = 1$, $\beta = 1$, and $\epsilon_e' = \epsilon_e$. Notice strong oscillations persist even at this layer.

are smoothed out. Observe that at the interior layers the density of states start showing some oscillatory behavior. For the sake of comparison, in Figs. 3 and 4, we plot the LDS for the first four layers for $\epsilon_e = -\epsilon_0 = 1$, $\beta = 1$, and $\epsilon_e' = \epsilon_e$ and $1.5\epsilon_e$, respectively. Since for these values the existence condition [Eq. (14)] for a surface state is no longer satisfied, we do not obtain a state in the band gap. Otherwise, the density of states for the various layers show approximately the same structures in all these cases except for the fact that the peaks in the LDS for the conduction band are somewhat enhanced in Figs. 3 and 4.

As we get into the crystal, we would expect that the LDS would start to resemble the LDS of a perfect infinite crystal. In order to check this point we have calculated the LDS for the 19th layer for $\epsilon_e = -\epsilon_0 = 1$, $\beta = 1$, and $\epsilon_e' = \epsilon_e$, which is shown in Fig. 5. We notice that even at this layer, the LDS shows very strong "resonance"-like oscillatroy structure and has no resemblance to the LDS of a perfect crystal except for the envelope. This oscillatory behavior can be attributed to an interference effect owingto surface scattering. Such an interpretation of the oscillatory behavior can be verified by reexamining the local Green's function at the mth layer which is given by (Eq. 7)

$$G(m, m) = \bar{G}(0, 0)(1 + e^{i(m+1)\theta}), \quad m \text{ even} \qquad (20a)$$

$$= \frac{E - \epsilon_e}{E - \epsilon_0}\bar{G}(0, 0)(1 - e^{i(m+1)\theta}), \quad m \text{ odd}, \qquad (20b)$$

where

$$e^{i\theta} = \tfrac{1}{2}[\alpha + i(4 - \alpha^2)^{1/2}] \text{ if } \epsilon < E < (\epsilon^2 + 4\beta^2)^{1/2} \qquad (21a)$$

$$= \tfrac{1}{2}[\alpha - i(4 - \alpha^2)^{1/2}] \text{ if } -(\epsilon^2 + 4\beta^2)^{1/2} < E < \epsilon\,. \qquad (21b)$$

Here we have let $\epsilon = \epsilon_e = -\epsilon_0$. From Eqs. (20a)–(20b) we derive the condition for $G(m, m) = 0$ as

$$e^{i(m+1)\theta} = -1, \quad m \text{ even} \qquad (22a)$$

and

$$e^{i(m+1)\theta} = 1, \quad m \text{ odd}. \qquad (22b)$$

Thus the values of $\theta[\equiv \theta_n(m)]$ for which $G(m, m) = 0$ (except those at the band edges) are given by

$$\theta_n(m) = \frac{(2n+1)\pi}{m+1},$$

where (23a)

$n = 1, 2, \ldots (\tfrac{1}{2}m - 1)$ for m even

and

$$\theta_n(m) = \frac{2n\pi}{m+1},$$

where (23b)

$n = 1, 2, \ldots [(m-1)/2]$ for m odd.

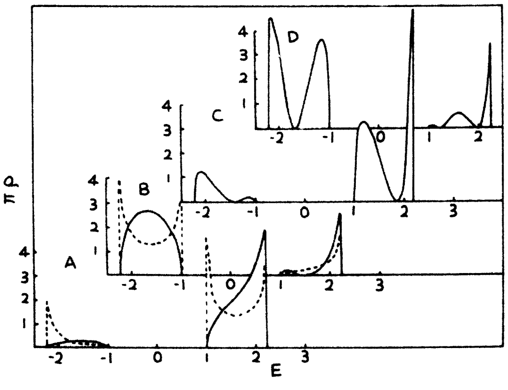

FIG. 4. Local density of states for the first four layers for $\epsilon_e = -\epsilon_0 = 1$, $\beta = 1$, and $\epsilon_e' = 1.5\,\epsilon_e$.

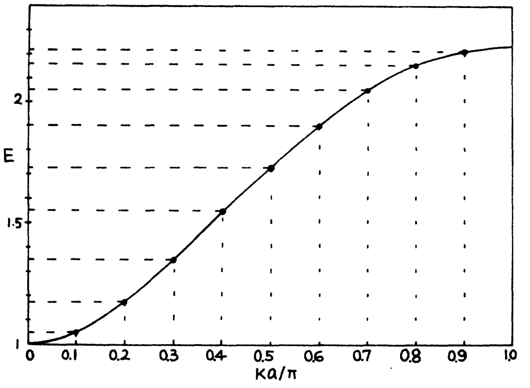

FIG. 6. Energies $E_n(m)$ and the wave numbers k_n associated with the local "pseudo energy gaps" (indicated by the dots) in the LDS (upper band) for the 19th layer.

Using Eqs. (11) and (21)–(23) we obtain the energy values

$$E_n(m)=\pm[\epsilon^2+2\beta^2+2\beta^2\cos\theta_n(m)]^{1/2}, \qquad (24)$$

at which both the real and imaginary parts of the local Green's function $G(m, m)$ at the mth-site vanish. Note that these energy values vary from site to site and their total number at a particular site is determined by Eq. (23).

For the sake of comparison, we recall that the energy dispersion for the perfect crystal in this model is given by

$$E=\pm[\epsilon^2+2\beta^2-2\beta^2\cos(2\pi a/\lambda)]^{1/2}, \qquad (25)$$

where λ is the electronic wavelength. The band edges for such a crystal at which the Bragg-diffraction condition is satisfied, are given by the condition

$$ka\equiv\frac{2\pi}{\lambda}\,a=\pm\pi.$$

By comparison we see that for the cleaved crystal the same criterion is satisfied by Eq. (24), which can be written as

$$\begin{aligned} n'\lambda&=(m+1)a, \quad m \text{ odd} \\ (n'+\tfrac{1}{2})\lambda&=(m+1)a, \quad m \text{ even}, \end{aligned} \qquad (26)$$

where $n'=m+1-2n$ and possible values of n are given in Eq. (23). Equation (26) thus represents the Bragg-like conditions which define certain local "pseudo energy gaps" that occur within the allowed bands of the perfect crystal, because of the presence of the surface. We can also calculate the number of these local "pseudo energy gaps" or energies at which the surface Green's function goes to zero in the upper (conduction) and the lower (valence) bands from Eqs. (23a), (23b), and (24). We notice that each $\theta_n(m)$ corresponds to two zeros (one in the conduction band and one in the valence band) of the Green's function. Thus we conclude that there are $m-2$ ($m\geqslant 3$) zeros (excluding those at the band edges) for the even layers and $m-1$ zeros for the odd layers. All these features show up in the numerical calculations as demonstrated in Figs. 3 and 5. The energies of the local "pseudo energy gaps" and their associated k_n's ($=2\pi/\lambda_n$) are plotted in Fig. 6 which illustrate the consequences of the Bragg-like conditions [Eq. (26)]. As mentioned before the conditions (23a) and (23b) do not include the conditions on the band edges at $E=\pm\epsilon$ and $\pm(\epsilon^2+4\beta^2)^{1/2}$, which we now consider more carefully. At these band edges we can calculate analytic properties of the LDS exactly. At the inner band edges, i.e., at $|E|\gtrsim\epsilon$ the density of states given by Eqs. (8), (20a), and (20b) can be shown to be

$$\rho_m=-\frac{2}{\pi}\,\mathrm{Im}[\overline{G}(0,0)]=\frac{1}{\pi\beta}(E-\epsilon)^{-1/2}(E+\epsilon)^{1/2}, \quad m \text{ even} \qquad (27)$$

$$\rho_m=\frac{1}{\pi}\,\frac{(m+1)^2}{4\beta^3}(E-\epsilon)^{3/2}(E+\epsilon)^{1/2}, \quad m \text{ odd}.$$

As shown in Figs. 3 and 5, at the upper edge of the valence band, i.e., at $E=-\epsilon$, the shape of the LDS is determined by $(E+\epsilon)^{1/2}$ at all layers; at the lower edge of conduction band, i.e., at $E=\epsilon$, the LDS varies as $(E-\epsilon)^{3/2}$ at all odd layers and has

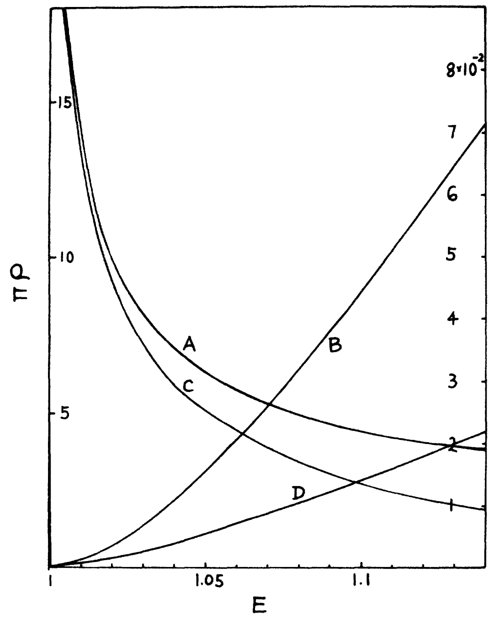

FIG. 7. Blowup of Fig. 3 in the vicinity of $E=\epsilon$. The scale for curves A and C (representing the zeroth and second layer) is on the left and that for the curves B and D (representing the first and third layer) is shown on the right.

a singularity of the type $(E-\epsilon)^{-1/2}$ at all even layers. The blowups of LDS in the vicinity of $E=\epsilon$ for the first four layers have been shown in Fig. 7.

At the outer edges, i.e., at $E=\pm(\epsilon^2+4\beta^2)^{1/2}$, the LDS can be shown to vary as $(\epsilon^2+4\beta^2-E^2)^{1/2}$ at all layers as depicted in Figs. 3 and 5.

The criterion for $G(m, m)=0$ will however be modified when the surface perturbations $V(0, 0)$ are no longer negligible. As shown in Figs. 2 and 4, the oscillatory structures in LDS still persist, but at shifted energies, and it can be shown that the real and imaginary parts of $G(m, m)$ do not vanish simultaneously. This strong oscillatory behavior in the LDS should persist even in a three-dimensional crystal if the LDS is measured at the surface with a fixed wave vector $k_{\parallel}$ in a direction parallel to the surface.

III. CONCLUSIONS

In this paper we have applied the surface Green's-function theory to study a semi-infinite one-dimensional ionic crystal and have been able to compare the Green's-function theory with the conventional LCAO method. We have shown that as far as the energies and the decay constant of the surface state are concerned, these two theories produce exactly the same results.

The Green's-function theory also allows us to study the properties of the bulk states. Our study shows a strong oscillatory behavior of the LDS for a one-dimensional crystal. We have also shown that in the absence of the surface perturbation, not only the LDS oscillates but the entire local Green's function (both real and imaginary parts) goes to zero whenever a Bragg-like condition is satisfied. We attribute this oscillatory phenomenon to an interference effect due to surface scatterings and show that certain local "pseudo energy gaps" would appear at those values of E at which the Bragg-like conditions are satisfied. Thus these oscillatory features should, in principle, persist infinitely deep into the crystal. But the observability of such oscillations in any experiment would be limited by the imperfections of the lattice, the resolution of the instruments, and the presence of other bands which have not been considered in the present model. It should be mentioned here that the appearance of these "pseudo energy gaps" is strictly a local property and their effects will be smeared out in the average bulk density of states.

---

[1] I. Tamm, Phys. Z. Sowjetunion 1, 733 (1932).

[2] E. T. Goodwin, Proc. Camb. Philos. Soc. 35, 232 (1939).

[3] J. Koutecky, Phys. Rev. 108, 13 (1957).

[4] J. Koutecky and M. Tomasek, Phys. Rev. 120, 1212 (1960).

[5] D. Kalkstein and P. Soven, Surf. Sci. 26, 85 (1971).

[6] E-Ni Foo and H. S. Wong, Phys. Rev. B 9, 1857 (1974).

[7] R. Haydock and M. J. Kelly, Surf. Sci. 38, 139 (1973).

[8] J. D. Levine and P. Mark, Phys. Rev. 144, 751 (1966).

[9] J. D. Levine, Phys. Rev. 171, 701 (1968).

[10] J. D. Levine and S. G. Davison, Phys. Rev. 174, 911 (1968).