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Surface-induced charge disturbances in filled bands

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We have studied, both for the Kronig-Penney model and in general terms, the charge disturbance induced in a filled band of electrons by a solid surface. The existence of surface-charge quantization in a filled band is demonstrated and a division of energy bands into two types is made on this basis. The complementary role that surface state and band charge disturbances play in minimizing the total charge disturbance produced by the surface has been discussed and their respective dependence on bulk and surface parameters illustrated. In this connection the special character of midgap surface states and their relevance to self-consistent calculations has been established.

I. INTRODUCTION

The electron charge density in the vicinity of a metal surface has been the subject of much recent study.[1] Simple-model calculations for metal surfaces reveal the Friedel oscillations and asymptotic behavior of the charge disturbance expected for more realistic metals,[2] and serve as guides for calculations that attempt to derive fully self-consistent metal-surface charge densities.

In comparison with the situation for metal surfaces, there has been considerably less study of model calculations appropriate to semiconductors and insulators.[3]

It is the purpose of this paper to study in detail the charge disturbance in the vicinity of the surface of a semi-infinite Kronig-Penney (KP) model. This model has a venerable history[4] in the theory of surface states but to the authors's knowledge, no systematic study of the behavior of the surface charge density in this model has been undertaken. A number of general conclusions can be drawn that imply a considerably broader range of applicability of our results than just the KP model. Finally, the implications of these results for self-consistent calculations will be touched upon.

The organization of the remainder of the paper will be as follows. In Sec. II the KP-model notation is defined and both band and surface-state solutions to the Schrödinger equation obtained. In Sec. III the behavior of the charge disturbance for a filled band is analyzed for a general surface and bulk potential and the more specific results for the KP model discussed. Section IV contains the numerical results on the KP model and discusses the implications for self-consistent calculations.

II. KRONIG-PENNEY MODEL—ANALYTIC SOLUTIONS

The model potential studied is shown in Fig. 1. It is given by

$$V(x)=V\sum_{n=1}^{\infty}\delta(x-na)+U\theta(d-x)\,. \tag{2.1}$$

As a preliminary to writing down the solution to the semiinfinite KP model we list the solutions for the infinite solid. The wave function (for $V>0$) is given by

$$\varphi_k(x)=\alpha_n(k)\,e^{i\kappa(x-na)}+\beta_n(k)e^{-i\kappa(x-na)},\quad na\leq x\leq na+a\,, \tag{2.2}$$

where

$$\alpha_n=\sin[\tfrac{1}{2}(k+\kappa)a]\nu(k)e^{-i\kappa a/2}\,e^{ikna}, \tag{2.3a}$$

$$\beta_n=\sin[\tfrac{1}{2}(\kappa-k)a]\nu(k)e^{i\kappa a/2}\,e^{ikna}, \tag{2.3b}$$

and

$$\kappa=(2E)^{1/2}\,. \tag{2.4}$$

The relation between energy and wave vector is

$$\cos ka-\cos\kappa a=(Va/\kappa a)\sin\kappa a\,, \tag{2.5}$$

while the normalization fixes ν,

$$\nu^2(k)=\frac{1}{a}\left(\frac{Va}{(\kappa a)^2}\sin^2\kappa a+1-\cos\kappa a\cos ka\right)^{-1}\,. \tag{2.6}$$

The Bloch wave vector is denoted by k, running from $-\pi/a$ to π/a.

From Eqs. (2.2)–(2.6) the solutions to the semiinfinite KP model are constructed. For the band states

$$\Psi=\begin{cases}(1/\sqrt{2})(\varphi_k e^{i\omega}+\varphi_k^* e^{-i\omega}), & x\geq d\\ Ae^{L(x-d)}, & x\leq d\end{cases} \tag{2.7}$$

where

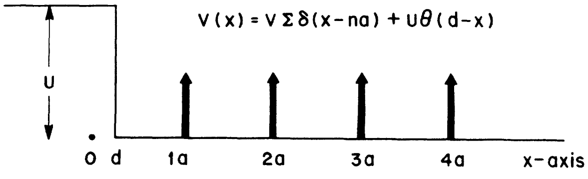

FIG. 1. Potential is plotted vs distance x for a semiinfinite abrupt junction KP model.

$$L = [2(U-E)]^{1/2} . \tag{2.8}$$

The scattering phase shift ω is determined from continuity of the logarithmic derivative at $x=d$,

$$e^{2i\omega_k} = \left. \frac{\varphi_k'^{*} - L\varphi_k^{*}}{L\varphi_k - \varphi_k'} \right|_{x=d} , \tag{2.9}$$

where

$$\varphi_k' = \frac{d}{dx} \varphi_k . \tag{2.10}$$

Surface states, when they exist, are given by

$$\Psi = \begin{cases} B\varphi_k(x), & x \geq d \qquad (2.11) \\ C e^{L(x-d)}, & x \leq d \qquad (2.12) \end{cases}$$

where φ_k is given by (2.2) and k has the form

$$ak = ial + \binom{0}{\pi} \quad (l > 0) \tag{2.13}$$

The necessary and sufficient condition for the existence of a surface at an energy $\kappa = (2\epsilon)^{1/2}$ is that κ lie in a band gap of the bulk KP model and that the equality

$$(2U-\kappa^2)^{1/2} = -\kappa \left[\tanh\frac{la}{2} + \tan\frac{\kappa a}{2} \tan\frac{\kappa a}{2}\left(\frac{2d}{a}-1\right) \right] \times \left[\tan\frac{\kappa a}{2} - \tanh\frac{la}{2} \tan\frac{\kappa a}{2}\left(\frac{2d}{a}-1\right) \right]^{-1} \tag{2.14}$$

be satisfied, where

$$\cosh al = \left| \cos\kappa a + \frac{Va}{\kappa a} \sin\kappa a \right| . \tag{2.15}$$

The constants B and C are fixed by continuity at $x = d$ and normalization and are not listed here for brievity.

All the above equations are equally valid for V attractive and $E > 0$. For $E < 0$, one can still use (2.2)-(2.25), but κ is now imaginary.

III. CHARGE DISTURBANCE—GENERAL DISCUSSION

The electron density in a band is just

$$\rho_B(x) = \frac{a}{\pi} \int_0^{\pi/a} dk \left| \Psi_k(x) \right|^2 , \tag{3.1}$$

where a is the lattice constant normal to the surface. For a surface state it is just

$$\rho_s(x) = \left| \Psi_s(x) \right|^2 . \tag{3.2}$$

These two quantities will be our main focus of attention. We begin by summarizing the results of our numerical studies on the KP model and placing them in a more general context. Consider first

$$N_B(n) = \int_{-\infty}^{na} \rho_B(x)\, dx , \tag{3.3}$$

the total number of electrons per spin in a band to the left of a delta function at $x=na$. For a filled band this quantity is asymptotically quantized,

$$N_B(n) - n \xrightarrow[n\to\infty]{} c , \tag{3.4}$$

where c is a constant. Our principal result is that c must be integral or half-integral, independent of details of the surface potential. This result is expected to hold for any completely filled band of states which is separated from any other bands of states by a finite energy gap.[5] A related electron quantization rule has been proved by Heine[3] for a one-dimensional finite slab within the nearly free electron approximation. A general proof we believe can be constructed from the work of Appelbaum and Blount,[6] in particular from their Eq. (2.30) for the integrated charge density, if the stationary nature of the wave functions in vicinity of band edges is taken into account. In that case the phase shifts are integral multiples of $\frac{1}{2}\pi$, from which the charge quantization follows. The details of this argument will be reserved for future publication.

We find that the type of quantization obeyed depends on the energy band in question, some bands having $N_B - n \rightarrow m + \frac{1}{2}$, and other $N_B - n \rightarrow m$, m being an integer. The latter type of behavior is the more common in the KP model, occurring for all bands in the repulsive delta function case ($V > 0$) and all save the lowest band for the case $V < 0$.

The physical distinction between the two classes of band is readily discerned. A band in the "half-integral" class, which will be referred to as atomic, is derived from atom states localized on the attractive δ functions. This is the conventional band usually discussed in solid state textbooks. There is only one such band in the δ-function KP model for the obvious reason that a δ function is capable of binding only one state.

A band in the "integral" class, which we call molecular, has its origin in an adjacent pair of δ functions. In isolation, a pair of δ functions will support resonant states, whether the δ functions are repulsive or attractive. It is from these resonant states that the bulk bands derive. Those below the vacuum level are contained within the solid by the surface barrier in our model.

We are now in a position to understand the two types of quantization that occur. Consider the case for which $V < 0$. The lowest band is derived from states located on the δ functions. When we integrate the band charge up to a δ function we are including a half-integral number of atomic states. For the next band, derived from states located between δ functions, we include an integral number of states integrating to the δ function. An integral number are also contained in the "molecule" formed by the end δ function and the surface barrier. It is this simple counting argument which accounts for the difference between the bands.

Having discussed the asymptotic limit of the charge in a band, we consider the nature of the charge disturbance near the surface, that is, the small-n behavior of $N_B - n$. In contradistinction to a metal, the disturbance falls off exponentially rather than as a simple power law. This result is quite general and can be seen from an analytic analysis of the integrand in (3.1).

A very similar analysis has recently been published by Rehr and Kohn in the course of studying the properties of Wannier functions defined for a one-dimensional semi-infinite solid.[8] We refer the reader to their paper for the details of the analysis, whose key features we describe below.

The integration in (3.1) can be extended from $-(\pi/a)$ to (π/a), and the integration contour can subsequently be deformed into the complex k plane. Since the Bloch waves entering the scattering state contain a exponential factor e^{ikx}, the decay rate of the disturbance is determined by the maximum value of Imk to which the contour can be deformed. This is limited by the analytic properties of the integrand in (3.1). It is true in general that one-dimensional Bloch states, considered as analytic functions of k, have branch points at finite values of Imk which depend on the band in question. These branch points correspond to real energies near the center of the band gaps, and encircling the branch point takes one to another Riemann sheet corresponding to the next band.[8] This behavior can be shown in the case of the KP model by examining the analytic behavior of the transcendental equation (2.5).

These branch points set the ultimate limit on the rate at which the disturbance can heal. However, it may not be possible to achieve this rate. If a surface state occurs at an energy near the band under consideration, the integrand in (3.1) will have a pole at a value of Imk corresponding to the decay rate of the surface state. This pole then limits the deformation of the integration contour, and a much longer ranged disturbance may result.

It can be shown[8] that if instead of just the band charge, one considers the disturbance in the sum of the band charge plus surface state charge, the pole in the integrand of (3.1) is cancelled, and the branch point determined by the bulk band structure once again becomes the singularity setting the decay rate.

The analysis of (3.1) only determines the asymptotic rate of decay of the disturbance. It gives neither the amplitude of the asymptotic term nor the depth into the solid required to reach the asymptotic form. For a band plus an adjacent surface state, we find a general trend for the disturbance amplitude in the layers near the surface that can be rationalized, if not proved, from the analytic picture. If the surface barrier potential is changed continuously, the surface state can be swept across its gap, say from band 1 to band 2. Its charge density, and that in both bands must change continuously.[9] Near either edge of the gap, the surface state charge can cancel the pole contribution in the integral for the charge in the adjacent band. When it is precisely at the energy corresponding to the branch point-a situation in no way physically pathological—we might expect it to be shared, that is, for half its amplitude to cancel the disturbance in band 1, and half to cancel the disturbance in band 2. That this in fact occurs is strikingly demonstrated by the numerical examples. For other energies near the center of the gap, continuity leads us to expect that the surface state will cancel the sum of the disturbances in bands 1 and 2, but that no simple fraction of the surface state should cancel the disturbance in either band independently. This observation is at variance with a simple interpretation of the analysis in terms of the singularities of the integrand in (3.1), which suggests that the "ownership" of the surface state changes discontinuously from band 1 to band 2 as the surface state pole changes Riemann sheets.[10]

Before proceeding to those numerical examples we should like to comment upon the extension of the above observations to three dimensions. In that case it is convenient to decompose $\vec{k}$, now a three-dimensional vector, into $\vec{k}_\parallel$, parallel to the surface, and k_z normal to the surface. For fixed $\vec{k}_\parallel$, we often have one-dimensional bands similar to those studied in the model, that is, isolated bands with monotonic E vs k. For these cases, the conclusions derived from our model should apply.

The charge quantization condition should thus be satisfied on a $\vec{k}_\parallel$-by-$\vec{k}_\parallel$ basis. Whether a particular band has "integral" or "half-integral" quantization can be determined by examining the spatial distribution of the charge associated with the band in question. If the charge is centered on atoms or bonds that lie wholly between the set of planes parallel to the surface plane and separated by the normal projection of the primitive basis vectors, we expect "integral" quantization. If these planes cut the center of the charge distribution, we expect "half-integral" quantization. For the Si (111) surface, for example, we have observed half-integral quantization for the valence band forming the bond which is broken when the surface forms, and integral quantization for the other three.[10]

The nature of the disturbance in the total charge is complicated by the $\vec{k}_\parallel$ integration. In general, there should be a superposition of exponentials, with the longest-range term set by the smallest band gap. A surface state can exist in part of the two-dimensional Brillouin zone and merge into a band elsewhere. We expect that moving a surface state into the band by gradual variation of the k_z band structure by the "parameter" $\vec{k}_\parallel$ should be equivalent to doing so by varying the barrier potential for fixed k_z band structure. Our results then imply that the band plus surface state charge should be a smooth function of $\vec{k}_{\parallel}$ through this boundary of surface state existence.

Situations may arise in a three-dimensional band structure that do not have a one-dimensional analog, even for fixed $\vec{k}_{\parallel}$. A band may have a nonmonotonic E vs k_z, or two bands may overlap. In either case, there can be more than one reflected Bloch wave for a given incident Bloch wave. We believe that charge quantization will be obeyed on a band by band basis in the first case, and for the sum of the overlapping bands in the second.

IV. KP NUMERICAL RESULTS

We turn now to our numerical work. In presenting our results we shall work with dimensionless parameters

$$\begin{aligned}&\bar{k}=ka,\quad \bar{\kappa}=\kappa a,\quad \bar{V}=Va,\quad \bar{U}=Ua^2,\\&\bar{d}=d/a,\end{aligned}\tag{4.1}$$

where the bar shall be implicit henceforth. Substituting the scattering-state wave function, Eq. (2.7), in the band-charge density integral (3.1), we see that the difference between the charge of a given band in the infinite and semi-infinite KP model can be written

$$D(x)=\int_0^{\pi} dk\,\mathrm{Re}\left[e^{2i\omega_k}\varphi_k^2(x)\right]\ .\tag{4.2}$$

The integration over k in (4.2) was performed numerically after the change of variables

$$\int_0^{\pi} dk\rightarrow\int_{\kappa_-}^{\kappa_+} d\kappa\,\frac{dk}{d\kappa}\ ,\tag{4.3}$$

where $\kappa_{\pm}$ are the values of κ for a given band at $k=0$, π/a, respectively. In recognition of the $1/\sqrt{E}$ singularities in the one-dimensional density of states $dk/d\kappa\rightarrow\infty$ at $\kappa=\kappa_{\pm}$ we have used the numerical algorithm

$$\int_a^b\frac{f(y)\,dy}{[(y-a)(b-y)]^{1/2}}=\sum_{i=1}^{n}\frac{\pi}{n}f(y_i)\ ,\tag{4.4}$$

$$y_i=\frac{a+b}{2}+\frac{b-a}{2}\cos\left(\frac{2i-1}{n}\pi\right)\ .\tag{4.5}$$

It was found that this algorithm gave excellent results (1 part in 10^5) for $n\sim 400$.

In discussing our results we are faced with the difficulty that we are dealing with a system that, simple as it is, has four parameters: the barrier strength, its position relative to the surface δ function, the strength of the bulk potential, and finally the particular band of interest.

We first fix our surface parameters, $d=0.2$, and $U=25$ (for $a\sim 6$ this corresponds to a surface barrier of ~19 eV), and vary the bulk parameters, studying $V=.5$, 1.0, and 1.5 and the two lowest bands. The third band extends above vacuum.

The first and most striking feature, in many respects, is the quantization of surface charge for all cases studied. Consistent with the molecular nature of the bands the total charge to the left of a point $x=ma$ (m large) is just $(m-1)$. There is no extra charge introduced by the region between $-\infty$ and a over that in the infinite bulk to the right of $x=a$. While there is no net charge associated with this region there certainly is a charge disturbance. Charge leaks from the interior of the crystal out into the surface region, creating a charge deficit in the interior unit cells. We have tabulated the integrated charge deficit

$$D_n=\int_{na}^{(n+1)a} dx\,D(x)\ ,\tag{4.6}$$

for $n=1,\ldots,5$ in Table I, for the two lowest bands

TABLE I. Charge deficits per unit cell for the two lowest bands of three different crystal potentials $V=0.5$, 1.0, 1.5 are tabulated against unit-cell coordinate m, where m labels the unit cell $ma\leq x\leq(m+1)a$. An analogous tabulation is also made for the charge density in the surface states that split from each of the bands.

M	1	2	3	4	5	
Band I	−0.03851	−0.04604	−0.04928	−0.04946	−0.04790	$V=0.5$
S. state	0.08767	0.07917	0.07145	0.06451	0.05824	
Band II	−0.05513	−0.04582	−0.03962	−0.03556	−0.03277	
S. state	0.04612	0.04387	0.04173	0.03969	0.03776	
Band I	−0.09744	−0.09640	−0.08685	−0.07496	−0.06330	$V=1.0$
S. state	0.14790	0.12114	0.09923	0.08128	0.06657	
Band II	−0.08432	−0.06863	−0.06013	−0.05457	−0.05021	
S. state	0.08403	0.07614	0.06900	0.06252	0.05666	
Band I	−0.14520	−0.12457	−0.09887	−0.07602	−0.05761	$V=1.5$
S. state	0.18873	0.14089	0.10517	0.07851	0.05861	
Band II	−0.10811	−0.08823	−0.07675	−0.06785	−0.05998	
S. state	0.11518	0.09956	0.08607	0.07440	0.06931	

TABLE II. Square root of the energy $\kappa = (2E)^{1/2}$ at the first four band edges are tabulated versus bulk potential V along with the energy of the surface states split from the bands by a surface barrier at $d = 0.2$ and strength $U = 25$.

Band I		S. state	Band II		S. state	
κ_-	κ_+		κ_-	κ_+		
0.96018	3.14159	3.15006	3.43101	6.28319	6.28722	$V = 0.5$
1.30654	3.14159	3.15774	3.67319	6.28319	6.29101	$V = 1.0$
1.54272	3.14159	3.16474	3.87948	6.28319	6.29459	$V = 1.5$

and for all three V's. Note that the disturbance is not highly localized, that it decays most slowly for $V = 0.5$ and most quickly for $V = 1.5$, but that the net deficit in the interior is greater for $V = 1.5$ than for $V = 0.5$.

Each of these bands have surface states split off from them. The energy of these surface states are shown in Table II, along with the band edge energies. If these surface states were filled, they would create a positive charge disturbance in the interior which is also listed, unit cell by unit cell in Table I. Note the excellent cancellation that occurs between the band deficit and the excess contributed by the surface states. This cancellation, discussed in Sec. III, was also previously observed by Baraff and Appelbaum for a case in which states were split from the bottom of a partially filled band.[7]

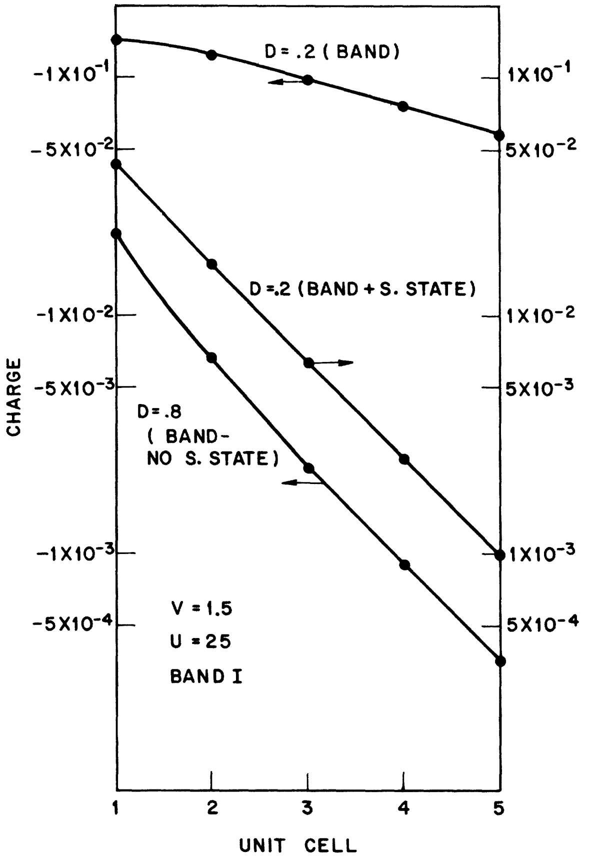

FIG. 2. Charge per unit cell between ma and $(m+1)a$, is plotted vs m for $m = 1, \ldots, 5$. Only the points are meaningful. For the band the charge deficit is plotted, and for the surface state contribution the total charge of the surface state is included. Band I is the lowest band with $V = 1.5$.

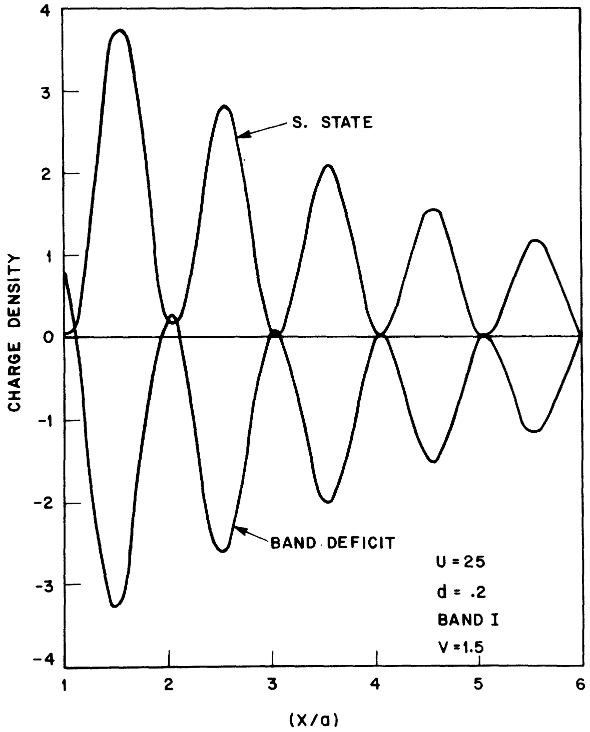

FIG. 3. Charge deficit in band I (lowest band) for $V = 1.5$ is plotted vs distance x along with the charge density in the surface state split from the band by a surface barrier whose parameters are $U = 25$, $d = 0.2$.

The cancellation is clearly better the wider the band gap and the narrower the band width. We have plotted the charge deficit in band I, $V = 1.5$ versus unit cell number on a semilog scale in Fig. 2. When the surface state is added, this deficit is dramatically cancelled. The remaining disturbance is of opposite sign, more than an order of magnitude smaller, and much more rapidly decaying. For comparison, we have plotted on the same scale the charge deficit present in the same band when the surface barrier is moved outward to $d = 0.8$. The band has no surface state split from it in this case and has a charge disturbance two orders of magnitude smaller than previously. Note that the fall off rate for the charge disturbance of the band plus surface state for the case $d = 0.2$ and of the band alone for $d = 0.8$ are numerically identical. This rate is fixed by the critical point structure in κ vs

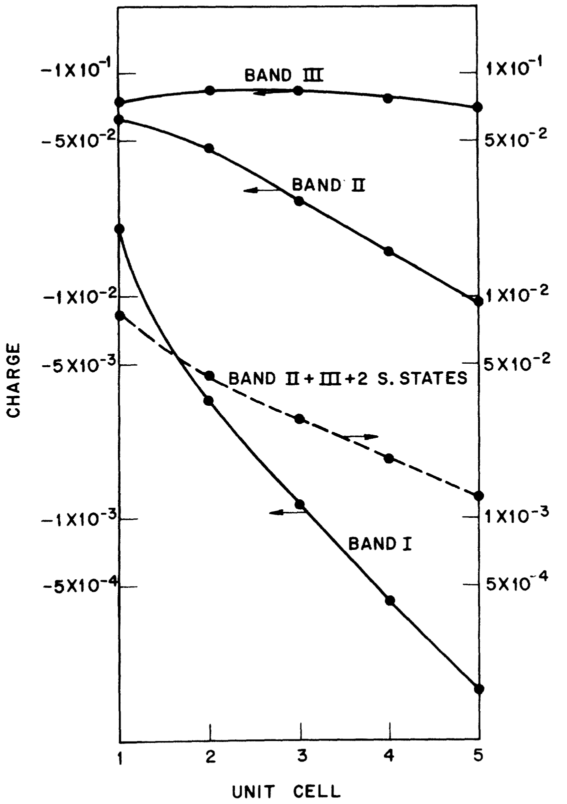

FIG. 4. Charge per unit cell between ma and $(m+1)\,a$, is plotted vs m for $m=1, \ldots, 5$. Only the points are meaningful. For the band the charge deficit is plotted, for the surface state contribution the total charge for the surface state is included. Bands I, II, and III labeled the three lowest energy bands, in order of increasing band energy.

k, as already discussed.

The cancellation between the surface state charge and the band charge deficit is also excellent point by point, as can be seen from a study of Fig. 3. The charge density of the surface state and the charge deficit in the band are plotted vs x to the right of the first δ function.

The relationship between surface-state charge density and band charge need not always be so simple. If we study the case $V=1.5$, $d=0.8$, and $U=50$, we find that the surface state split from band II does not cancel the charge-density deficit in that band. What has happened is that the surface state has moved close to band III, causing a charge disturbance in both bands II and III. If we sum both bands II and III and the two surface states split from them the excellent cancellation we obtain in the previous cases is recovered (see Fig. 4). In this case, however, the cancellation of the charge point by point is not nearly so good as that shown in Fig. 2.

In all cases so far studied the net band charge has been an integral number. For the case of attractive δ functions one finds that the "atomic" lowest band has half-integral charge. For barriers at $d=0.2$ and $d=0.5$ the net band charge is $n+\frac{1}{2}$. For a barrier at $d=0.8$, the net band charge is $n-\frac{1}{2}$. The atomic state localized on the surface δ function has been removed from the band by the adjacent surface barrier. Similarly by moving the surface barrier back (toward vacuum) one can increase the net band surface charge. For $V>0$, moving the surface barrier to $x=0$ allows the band to acquire an extra charge, for $d=-1$, two extra charges, and so on. Clearly, one can never change the band charge in a nonintegral fashion for a fixed band.

The final topic we wish to illustrate is the behavior of the charge disturbance as one varies the surface barrier in such a way as to sweep a surface state from one band through midgap toward the second band. We demonstrate this using the lowest band for $V=0.5$ and a surface barrier at $d=0.5$. Three surface-barrier heights, $U=6$, 10.369, and 25 are studied. The charge deficits for these three

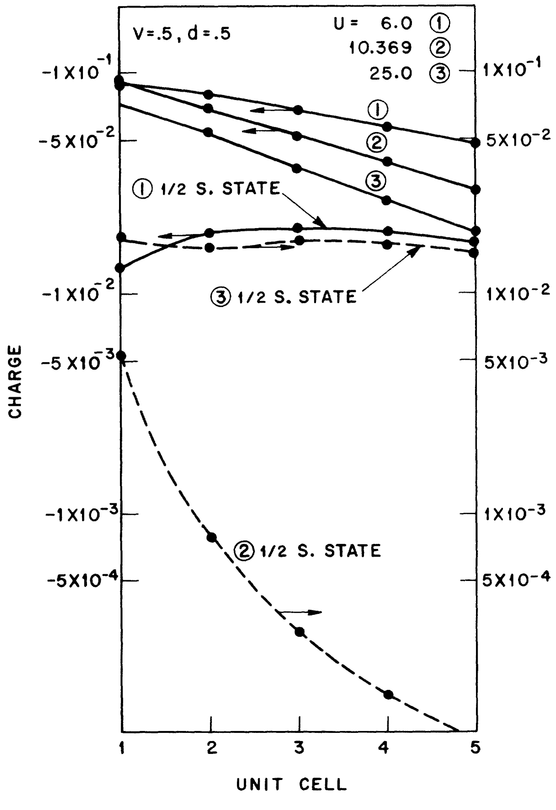

FIG. 5. Charge per unit cell for band I, $V=0.5$ is plotted versus unit cell index for three different surface barriers. The sum of charge per unit cell in a half-full surface state lying in the gap above band I and the charge in that band, is plotted vs unit-cell index.

cases are shown in Fig. 5. They scale in a very natural way, i.e., the stronger the surface barrier, the less charge leakage and therefore the smaller the long-range charge deficit. In each case, a surface state lies in the gap above the band of interest, at $\kappa = 3.189$, 3.286, 3.369, in order of increasing surface barrier. The intermediate κ value corresponds closely to midgap and is such that it coincides with the branch point that analytically joins the band to the one above it in energy.

In all cases the charge in the surface state considerably exceeds the band deficit, so the disturbance cancellation found previously will not occur. If, rather than adding the surface state charge density, one adds only half of it to the band charge, one finds a rather remarkable result, shown in Fig. 5. For the surface state lying near the critical gap energy, almost complete cancellation occurs between the band and surface state disturbances. For the two other cases, where surface states lie on either side of the critical point, the same procedure results in a total charge disturbance of considerable magnitude and range. There is a deficit for the lower energy state and an excess for the higher.

The underlying reason for this cancellation has been suggested in Sec. III; we shall comment here on a further physical implication of the behavior discussed.

The band of states contains $\frac{1}{2}$ a state less charge (per spin) than the number of δ functions present to the left of $x = ma$, m large, counting the δ function at the boundary as $\frac{1}{2}$. If we were to think of the δ functions carrying charge, one would, for "charge neutrality," half occupy the adjacent surface state (one-electron counting spin degeneracy). With the barrier adjusted so that the surface state lies above midgap, an electrostatic dipole is set up that would tend to lower the barrier. For a barrier adjusted to produce a surface state below midgap a dipole that tends to increase the barrier and push the surface state toward midgap occurs. Only for the surface state near midgap does no long-range charge disturbance in D_n occur. One has the following interesting result: the self-consistent potential tends to produce a midgap surface state. This appears to be the case for the occupied part of the surface-state band of Si (111). Of course, in three dimensions such behavior need only be true in a $\vec{k}_{\parallel}$-averaged sense.

A final point of qualification should be made here concerning the cancellation of the D_n and the surface-state charge. The charge deficit $D(x)$ does not cancel point by point with the surface state with comparable efficiency to that D_n achieves against the analogous surface state quantity. A full discussion of this must await a more complete analysis of the analytic behavior of the integrand in (4.2).

In summary, we have studied the behavior of the surface charge density—both for the KP model, as well as in general terms. We have discussed and illustrated the dependence of the charge density disturbance in a band on surface and bulk parameters and shown how that the disturbance is influenced by the presence of surface states. The existence of surface charge quantization in a filled band and its dependence on band type has also been discussed. Finally, the special character of a midgap surface state and its relevance to self-consistent calculations has been established.

We should like to acknowledge useful conversations with E. I. Blount, V. Heine, and L. Kleinman.

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