PHYSICAL REVIEW B VOLUME 9, NUMBER 10 15 MAY 1974

Three-dimensional model for surface states

G. Iadonisi and B. Preziosi

Istituto di Fisica Teorica dell'Università, Napoli, Italy

Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Recerche, Sezione di Napoli, Italy

(Received 27 March 1973; revised manuscript received 25 June 1973)

A detailed theoretical discussion of the surface bands in the Penn model is presented. It is found that a surface band always exists; another surface band may exist, if the gap is not too small and well below the vacuum level, but it plunges always in the valence band.

I. INTRODUCTION

It is well known that the surface-electron properties are better studied in semiconductors than in metals or in ionic crystals. In the metal case, in fact, the surface electrons cannot be distinguished from the bulk electrons, while in the ionic crystals it is practically impossible to obtain clean surfaces and crystals without impurities. The main surface-electron properties of a semiconductor compound are the number of the surface bands in the gap, their dependence on the surface momentum, and their connections with the optical and transport properties. The most interesting experimental and theoretical aspects of the problem have been recently reviewed by Davison and Levine.[1] Some experimental results[2,3] and numerical calculations[4] on the Penn model[5] indicate the presence of two surface bands. The question of the surface states in the Penn model is discussed in detail in this paper, as this model, although nonperiodic, seems suitable for the descriptions of the semiconductors properties, i.e., the q-dependent static dielectric constant,[5] which depend on the existence of a gap between the valence and conduction band. It is found that a surface band always exists; a second surface band, which always plunges in the valence band and gives small contribution to the surface properties, can exist only if the gap is not too small and well below the vacuum level. All the aspects of the problem are carefully and algebraically analyzed.

II. MODEL

The theory of the surface states has been recently simplified by the approach of Garcia-Moliner and Rubio.[6] It will be useful to give here a brief account of their method. We suppose that the crystal extends in the region $z>0$, that the periodic potential $V(\vec{r})$, defined in the whole space, is symmetric with respect to the plane $z=0$ and has mean value equal to zero and that the vacuum level is E_0. Our problem consists, then, in solving the Schrödinger equation

$$-\nabla^2\psi(\vec{r})+\theta(z)V(\vec{r})\psi(\vec{r})+\theta(-z)E_0\psi(\vec{r})=E\psi(\vec{r}), \tag{1}$$

where $\theta(z)$ is the step function and natural units ($\hbar^2=2m=1$) are used.

In the approach of Garcia-Moliner and Rubio[6] it is essential to know the Green's functions of the infinite crystal and of the vacuum, defined by

$$(-\nabla^2-E)G(\vec{r},\vec{r}\,')+V(\vec{r})G(\vec{r},\vec{r}\,')=\delta(\vec{r}-\vec{r}\,'), \tag{2}$$

$$[-\nabla^2-(E-E_0)]G_0(\vec{r}-\vec{r}\,')=\delta(\vec{r}-\vec{r}\,'). \tag{3}$$

We multiply Eq. (1) by $G(\vec{r},\vec{r}\,')$ and Eq. (2) by $\psi(\vec{r})$, subtract the resulting equations, apply to this difference the Green's lemma once in the volume $z>0$ and once in the volume $z<0$. If the energy is in a gap of the band structure of the crystal the following equations result

$$\psi(x,y,z)=-\int dx'\,dy'\,[G(x,y,z;x',y',0)\psi_{z'}(x',y',0)-G_{z'}(x,y,z;x',y',0)\psi(x',y',0)]\,,\quad z>0 \tag{4a}$$

$$0=\int dx'\,dy'\,[G(x,y,z;x',y',0)\psi_{z'}(x',y',0)-G_{z'}(x,y,z;x',y',0)\psi(x',y',0)]\,,\quad z<0\,. \tag{4b}$$

The application of the same procedure to Eqs. (1) and (3) gives, if the energy is below the vacuum level,

$$0=\int dx'\,dy'\,[G_0(x,y,z;x',y',0)\psi_{z'}(x',y',0)-G_{0z'}(x,y,z;x',y',0)\psi(x',y',0)]\,,\quad z>0 \tag{4c}$$

$$\psi(x,y,z)=\int dx'\,dy'\,[G_0(x,y,z;x',y',0)\psi_{z'}(x',y',0)-G_{0z'}(x,y,z;x',y',0)\psi(x',y',0)]\,,\quad z<0\,. \tag{4d}$$

The continuity of $\psi(\vec{r})$ and of its derivative $\psi_z(\vec{r})$ on the surface $z=0$ is automatically verified if Eqs. (4) hold. Equations (4a) and (4d) define ψ in the whole space in terms of the expressions of $\psi(\vec{r})$ and of $\psi_z(\vec{r})$ on the surface. These last quantities are determined by Eqs. (4b) and (4c), which give, furthermore, the surface bands.

The symmetry of $V(\vec{r})$ with respect to the plane

$z=0$ implies that

$$\left[\int dx'\,dy'\,G_{z'}(x,y,z;x',y',0)\psi(x',y',0)\right]_{z=0\pm}=\mp\tfrac{1}{2}\psi(x,y,0)\,. \tag{5}$$

Using (5) and the analogous relation for G_0, we obtain finally

$$\int dx'\,dy'\,[G(x,y,0;x',y',0)+G_0(x,y,0;x',y',0)]\psi_{z'}(x',y',0)=0\,, \tag{6}$$

which is the fundamental equation of Garcia-Moliner and Rubio.[6]

What has been told till now is completely general. However, the use of Eq. (6) requires the knowledge of the Green's function of the perfect crystal. As this function is not known, we will calculate it in the Penn model,[5] which makes use of the three-dimensional spherical forms of the Bloch functions and of the band structure of the one-dimensional nearly-free-electron model and which is slightly different from the three-dimensional cubic nearly-free-electron model.[7] This Penn model was very successful in describing the q dependence of the static dielectric constant in semiconductors. Its essential advantage consists in its resembling a band structure which has a gap and is quadratic near the gap.

The band structure and the three-dimensional spherical forms of the Bloch functions and of the one-dimensional nearly-free-electron model, in which the periodic potential is treated perturbatively, are

$$E(k)=\frac{1}{2}\left(k^2+\left(1-\frac{2k_F}{k}\right)^2k^2\pm\left\{\left[k^2-\left(1-\frac{2k_F}{k}\right)^2k^2\right]^2+16k_F^4\Delta^2\right\}^{1/2}\right), \tag{7}$$

$$\psi(\vec{\mathrm{k}},\vec{\mathrm{r}})=A_0(k)\,e^{i\vec{\mathrm{k}}\cdot\vec{\mathrm{r}}}+A_1(k)\,e^{i(1-2k_F/k)\vec{\mathrm{k}}\cdot\vec{\mathrm{r}}}\,, \tag{8a}$$

where

$$A_0(k)=\left(1+\frac{[E(k)-k^2]^2}{4\Delta^2k_F^2}\right)^{-1/2},\qquad A_1(k)=\frac{E(k)-k^2}{2\Delta k_F^2}A_0(k)\,. \tag{8b}$$

In the above equations k_F is the radius of the Brillouin zone and $k=|\vec{\mathrm{k}}|$. From now on, the momentum and energy will be measured in units k_F and k_F^2, respectively, and then from Eq. (7) the energy gap will become equal to 4Δ.

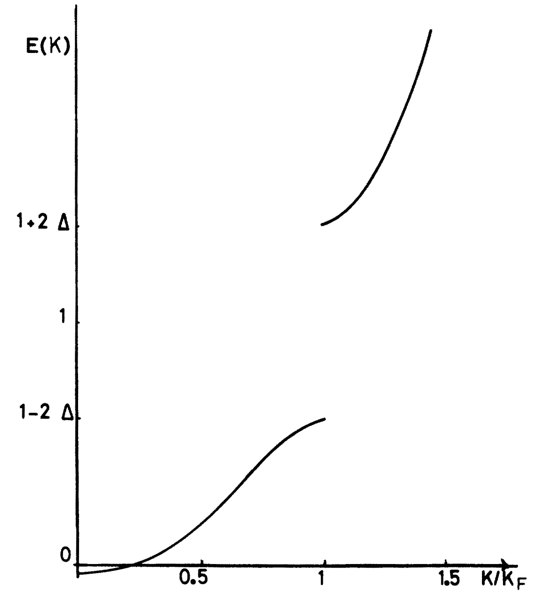

FIG. 1. Energy band structure in the Penn model. The value of Δ is 0.2.

The signs + and – in (7) indicate the upper and lower bands, respectively, which are shown in Fig. 1. Note that the lower band does not have a minimum at $k=0$, but at $k=1-(1-\Delta^2)^{1/2}$; the value of $E(k)$ at this minimum is equal to $-\Delta^2$ and is very close, for $|\Delta|<1$, to the value $2[1-(1+\Delta^2)^{1/2}]$, which the energy band (7) has at $k=0$. This value is lower than the maximum of the lower band at $k=1$ only if $|\Delta|<\frac{3}{4}$. If $|\Delta|\ll 1$, the fact that the minimum is not at $k=0$ is irrelevant and the results obtained using the band structure (7) do not differ from those which one would obtain using a band structure similar to (7) but with the minimum at $k=0$. On the other hand, only if $|\Delta|\ll 1$ the Penn model is compatible with its nearly free origin. In these conditions the energy gap is much smaller than the lower-band width, as is the case for semiconductors. Moreover, as $A_1(k)$ is important only when k^2 differs from 1 for less than Δ, Eq. (8a) can be approximated by

$$\psi(\vec{\mathrm{k}},\vec{\mathrm{r}})=A_0(k)\,e^{i\vec{\mathrm{k}}\cdot\vec{\mathrm{r}}}+A_1(k)\,e^{-i\vec{\mathrm{k}}\cdot\vec{\mathrm{r}}}\,. \tag{9}$$

Using this expression, Eq. (6) becomes

$$\alpha(q)\phi(\vec{\mathrm{q}})+\beta(q)\phi(-\vec{\mathrm{q}})=0\,, \tag{10}$$

where

$$\alpha(q)=\int_{-\infty}^{\infty}dk_z\left(\frac{1}{q^2-k_z^2-E+E_0}+\frac{1}{E(q,k_z)-E}\right),\qquad \beta(q)=2\int_{-\infty}^{\infty}dk_z\,\frac{A_0[(q^2+k_z^2)^{1/2}]A_1[(q^2+k_z^2)^{1/2}]}{E(q,k_z)-E}\,, \tag{11}$$

and $\phi(\vec{\mathrm{q}})$ is the two-dimensional Fourier transform of $\psi_z(x,y,0)$. Equation (9) is the essential approximation we use in this treatment; its correctness is confirmed by the fact that only the values of $\vec{\mathrm{q}}$ and k_z such that $E(q,k_z)=E$ (and E is in the gap) are important. Equation (10) admits solutions only when

$$\alpha(q)\pm\beta(q)=0\,, \tag{12}$$

the signs + and − referring, respectively, to the symmetric $[\phi(\vec{q})=\phi(-\vec{q})]$ and to the antisymmetric states $[\phi(\vec{q})=-\phi(-\vec{q})]$. Equation (12) gives the surface bands, that is to say, the energy as a function of q, which is the counterpart of the surface momentum. From Eqs. (7), (8b), (9), (11), and (12), the explicit form of the surface bands equations are, for $q<1$,

$$F^{\pm}(E,q)=\int_0^{\infty}\frac{dk}{q^2+k^2+E_0-E}+\int_q^1\frac{k\,dk}{(k^2-q^2)^{1/2}}\times\frac{1\mp\Delta/f(k)}{[1-f(k)]^2-(E+\Delta^2)}+\int_1^{\infty}\frac{k\,dk}{(k^2-q^2)^{1/2}}\times\frac{1\pm\Delta/f(k)}{[1+f(k)]^2-(E+\Delta^2)}=0\,, \tag{13}$$

where $f(k)\equiv[(1-k)^2+\Delta^2]^{1/2}$.

It follows from Eqs. (13) and from the fact that, for any k,

$$[1-f(k)]^2<E+\Delta^2<[1+f(k)]^2\,,\quad 0<|\Delta|/f(k)<1 \tag{14}$$

that, for $q<1$, (a) if the energy is in the gap $(1-2|\Delta|<E<1+2|\Delta|)$ and $|\Delta|<\frac{3}{4}$, the second term on the right-hand side (r.h.s.) of Eq. (13) is negative, while the other terms are positive; moreover, this second term goes to zero when $q\to 1$; (b) if $\Delta>0$, then $F^{+}(E,q)>F^{-}(E,q)$; (c) all the terms on the r.h.s. of Eq. (13), and so $F^{\pm}(E,q)$, are increasing functions of the energy, for fixed q and Δ; (d) when $\Delta\to-\Delta$ the symmetric and the antisymmetric solutions interchange, as do the symmetries of the Bloch states at the edges of the band. As the sign of Δ is the same as the sign of the periodic potential at the surface, we can say that the symmetry of the surface state depends on whether the periodic potential is cut (at the surface) in a point of maximum or minimum, but the surface bands are independent of this cut.

For $q>1$, Eq. (12) takes a form quite similar to Eq. (13), except for the second term on the r.h.s. of Eq. (13), which is missing, and the third integral of Eq. (13), which goes from q to ∞. In this case, then, $\alpha(q)$ of Eq. (12) is always positive and no band exists. Because of (d), we can limit ourselves to consider, from now on, only the case $\Delta>0$.

In the symmetric case [upper signs in Eq. (13)], we have that, as $f(1)=\Delta$, (e) when E goes to its upper limit $1+2\Delta$, as $[1+f(k)]^2-(E+\Delta^2)$ goes to $[f(k)-\Delta][f(k)+2+\Delta]$, the third term on the r.h.s. of Eq. (13) becomes positively divergent, because the integrand has a pole at $k=1$, for any q; (f) when E goes to its lower limit $1-2\Delta$, $F^{+}(E,q)$ goes to $F^{+}(1-2\Delta,q)$, which is an increasing function of q (later on an explicit evaluation of this quantity is given). Moreover, $F^{+}(1-2\Delta,q)$ goes to a positive number, for any Δ, when q goes to 1, while, when q goes to zero, it becomes negative only if Δ is larger than the value $\bar{\Delta}$ such that $F^{+}(1-2\bar{\Delta},0)=0$ ($\bar{\Delta}$ depends on E_0). For $\Delta>\bar{\Delta}$, there is a value $\bar{q}$ (depending on Δ) such that $F^{+}(1-2\Delta,\bar{q})=0$. Also these last properties will be explicitly seen later.

The consequence of (e) and (f) is that, if $\Delta<\bar{\Delta}$, there is no symmetric surface band; if instead $\Delta>\bar{\Delta}$, there is a symmetric surface band, but it disappears and goes into the lower crystal band for $q>\bar{q}$.

In the antisymmetric case [lower signs in Eq. (13)], (e′) when E goes to its lower limit, the second term on the r.h.s. of Eq. (13), and then $F^{-}(E,q)$, becomes negatively divergent, as, for $E=1-2\Delta$, the integrand has a pole at $k=1$, for any q; (f′) at the opposite limit, $F^{-}(1+2\Delta,q)$ is a positive number for any Δ and q (see below).

The consequence of (e′) and (f′) is that there is an antisymmetric surface band for any Δ; this surface band remains in the gap for any $q<1$, because of (a) and (e′), going to the lower crystal band when q goes to 1.

From the previous conclusions, the antisymmetric surface band is greatly preferred to the symmetric one and, from (b), it is above the symmetric one. Before entering into the physical discussion of these facts, let us recall that the words symmetric and antisymmetric refer to the behavior of the states in the xy plane and that the Penn model, because of its spherical structure, is not a periodic model. Keeping this in mind, when $\Delta>0$, the periodic potential is repulsive at the origin; the symmetric states are then not preferred, as they imply a large probability for the presence of the electron at the origin; the antisymmetric states are instead preferred, because they require a lower presence of the electron in the region near the origin. Of course, the reverse happens when $\Delta<0$.

The previous results are fully accounted by the evaluation of $F^{\pm}(E,q)$, which can be done by using the following approximations, which are very good if g is regular and $q<1$:

$$\int_q^1 dk\,\frac{kg(k)}{(k^2-q^2)^{1/2}}=\frac{1}{(1-q^2)^{1/2}}\left(\frac{q(2+q)(1-q)}{2(1+q)}\,g(q)+\frac{q^2}{1-q^2}\int_q^1 dk\,(1-k)g(k)+\int_q^1 dk\,g(k)\right), \tag{15}$$

$$\int_1^{\infty} dk\,\frac{kg(k)}{(k^2-q^2)^{1/2}}=[1-(1-q^2)^{1/2}]\,g(q)+\int_1^{\infty}dk\,g(k)\,.$$

Using Eqs. (15) we have, for $\Delta>0$,

$$F^{+}(E,q)=\frac{\pi}{2(q^2+E_0-E)^{1/2}}+\frac{q(2+q)}{2(1+q)}\left(\frac{1-q}{1+q}\right)^{1/2}\frac{1-\Delta/f}{(f-1)^2-(E+\Delta^2)}+[1-(1-q^2)^{1/2}]\,\frac{1+\Delta/f}{(f+1)^2-(E+\Delta^2)}$$
$$+\frac{1}{(E+\Delta^2)^{1/2}}\Bigg(\frac{q^2}{2(1-q^2)^{3/2}}\left[(\beta^-)^2\ln\left(1+\frac{|\Delta|-f}{1-|\Delta|+(E+\Delta^2)^{1/2}}\right)+(\delta^+)^2\ln\left(1+\frac{f-|\Delta|}{|\Delta|+(E+\Delta^2)^{1/2}-1}\right)\right]$$
$$+\frac{1}{2}\,\frac{\beta^-}{\beta^+}\left[\left(1-\frac{1}{(1-q^2)^{1/2}}\right)\ln\frac{\beta^++\beta^-}{\beta^+-\beta^-}+\frac{1}{(1-q^2)^{1/2}}\ln\left|\frac{2(1-q+f)-(\beta^++\beta^-)^2}{2(1-q+f)-(\beta^+-\beta^-)^2}\right|\right]$$
$$-\frac{\delta^+}{\delta^-}\left\{\frac{1}{(1-q^2)^{1/2}}\arctan\frac{\delta^+}{\delta^-}-\arctan\left[\frac{1-q+f}{\delta^+\delta^-}+\frac{1}{2}\left(\frac{\delta^+}{\delta^-}-\frac{\delta^-}{\delta^+}\right)\right]-\arctan\frac{\delta^+}{\delta^-}-\arctan\frac{1}{2}\left(\frac{\delta^+}{\delta^-}-\frac{\delta^-}{\delta^+}\right)\right\}\Bigg) \tag{16}$$

where

$\beta^{\pm}=[1+(E+\Delta^2)^{1/2}\pm\Delta]^{1/2}$, $\delta^{\pm}=\{\Delta\pm[(E+\Delta^2)^{1/2}-1]\}^{1/2}$.

$F^-(E,q)$ is obtained from the right-hand side of Eq. (16) with the simple substitutions $\Delta\to-\Delta$, $\beta^+\leftrightarrow\beta^-$, $\delta^+\leftrightarrow\delta^-$. As, when $E\to 1+2\Delta$, $\delta^-\to 0$, and, when $E\to 1-2\Delta$, $\delta^+\to 0$, the properties (e) and (e′) follow, simply looking at the last terms containing the arctan's. From Eq. (13) and from these expressions for $F^+(E,q)$ or $F^-(E,q)$, it is possible to deduce the surface bands. In Fig. 2, the upper surface bands (antisymmetric case) are given for two values of E_0.

It follows from Eq. (16) that

$$F^{+}(1-2\Delta,q)=\frac{\pi}{2[q^2+E_0-(1+2\Delta)]^{1/2}}+\frac{q(1-q^2)^{1/2}}{(1+q)f(f-2+\Delta)}+\frac{1-(1-q^2)^{1/2}}{f(f+2-\Delta)}$$
$$+\frac{1}{2(1-\Delta)^{1/2}}\left[\left(1-\frac{1}{(1-q^2)^{1/2}}\right)\ln\frac{1+(1-\Delta)^{1/2}}{1-(1-\Delta)^{1/2}}+\frac{2(1-\Delta)q^2}{(1-q^2)^{3/2}}\ln\frac{2-\Delta-f}{2-2\Delta}\right.$$
$$\left.+\frac{1}{(1-q^2)^{1/2}}\ln\frac{[1+(1-\Delta)^{1/2}]^2-1+q-f}{1-q+f-[1-(1-\Delta)^{1/2}]^2}\right]. \tag{17}$$

$F^-(1+2\Delta,q)$ is obtained from Eq. (17) with the substitution $\Delta\to-\Delta$. From these expressions for F^+ and F^- at the extrema, the properties (f) and (f′) may be checked. Moreover, from Eq. (17), one can derive for what values of Δ and E_0 the lower surface band is allowed and what is the region it occupies in the q space. For any value of Δ, there is a minimum value of E_0 for which the lower band exists. This value can be evaluated by noting that $F^+(1-2\Delta,0)$, which can be easily obtained from Eq. (17), is well approximated, for small values of Δ, by

$$\frac{1}{2}\left(\frac{\pi}{[E_0-(1-2\Delta)]^{1/2}}-\frac{\Delta}{(1-\Delta)^{3/2}}\right).$$

If we recall the property (f), it is easily seen that the value $\bar{\Delta}$, for which the lower band begins to appear is approximatively equal to $(1+(E_0)^{1/2}/\pi)^{-1}$. The extension of the lower band for any value of Δ and E_0 is shown in Fig. 3; if, e.g., Δ is equal to 0.2, only the region in the E_0, q plane at the left of the curve $\Delta=0.2$ is allowed. It is seen that, for any Δ, only if the vacuum level is high enough the lower surface band exists; moreover, the width of this band, which is given, for a fixed E_0, by the value of q for which the curve corresponding to the given Δ reaches the value E_0, increases with E_0,

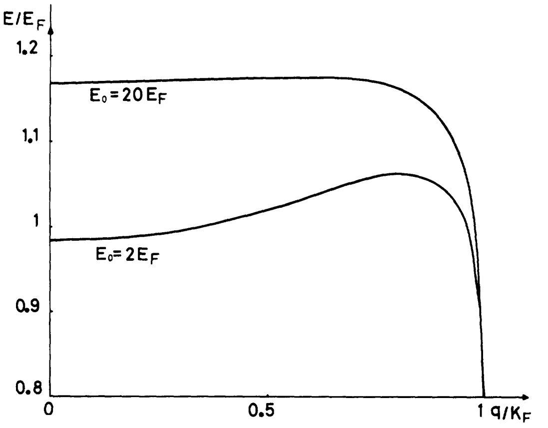

FIG. 2. Surface bands for the antisymmetric state with $\Delta=0.1$ and two different values of the vacuum level. E_F is the quantity $(\hbar^2/2m)k_F^2$.

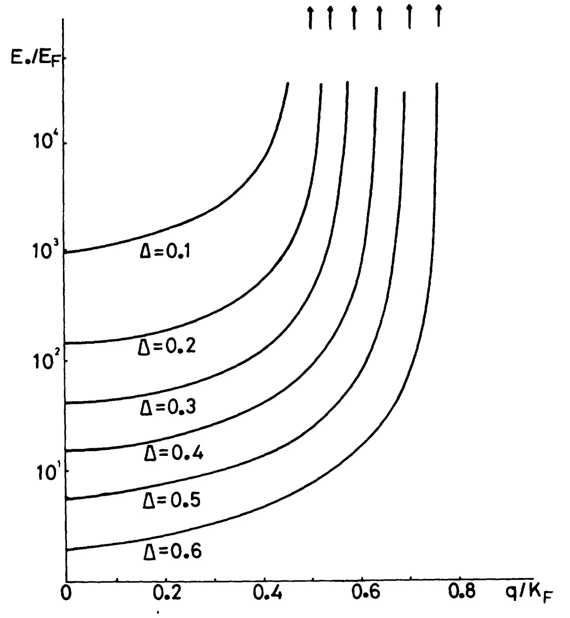

FIG. 3. Diagram of the minimum values of E_0 for which the lower band exists, for several values of Δ and for any q.

but for any Δ there is an asymptotic value of the width of the band. These asymptotic values are expressed, in the figure, by the arrows and correspond to the values for which $F^+(1-2\Delta, q)$ is equal to $\frac{1}{2}\pi(q^2+E_0-1+2\Delta)^{-1}$ [see Eq. (17)].

Finally, the expansion of $F^+(E, 0)$ near $E=1-2\Delta$, allows one to derive the value of the symmetric band at $q=0$. This value is approximately equal to

$$E=1-2\Delta+\Delta\left(\Delta(1-\Delta)^{1/2}-\frac{\pi(1-\Delta)^2}{(E_0-1+2\Delta)^{1/2}}\right). \tag{18}$$

If we take into account that this solution can be accepted only when the expression in large parentheses in Eq. (18) is positive, it follows that the symmetric band remains very close to the valence band. In fact from Eq. (18) we have $E-(1-2\Delta) < \Delta^2$.

The behavior of the gap between the surface bands is then essentially determined by the value of the antisymmetric band at $q=0$. This value $E(0)$ is plotted in Fig. 4 as a function of the vacuum level. This plot is interesting because the oxidation of the surface should correspond to an increase in the vacuum level.

It is interesting to note that the antisymmetric surface bands of Fig. 2 are well fitted, in the whole range (0, 1), by a curve of the form

$$E(q)=E(0)(1-q^2)^{1/2}(1+aq^2)+(1-2\Delta)q^2, \tag{19}$$

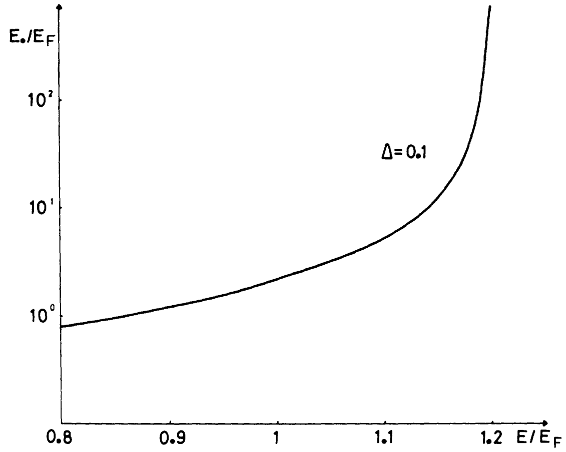

FIG. 4. Energy value at $q=0$ of the antisymmetric band as a function of the vacuum level with $\Delta=0.1$.

where $E(0)$ and a depend on Δ and E_0. For example, for $\Delta=0.1$ and $E_0=2$, $E(0)$ and a are given by 0.985 and -0.1, respectively. Equation (19) is quite useful to compute the density of surface states

$$n(E)=\frac{1}{2\pi}\int q\,dq\,\delta(E(q)-E)$$

$$=\frac{1}{2\pi}\sum_i\left|\frac{q}{dE(q)/dq}\right|_{E(q_i)=E}. \tag{20}$$

From Eqs. (19) and (20) it follows that, when $E=1-2\Delta$, $dE(q)/dq$ is infinite, so that $n(E)=0$; for increasing energy, there is only a value of q such that $E(q_i)=E$ until the energy reaches the

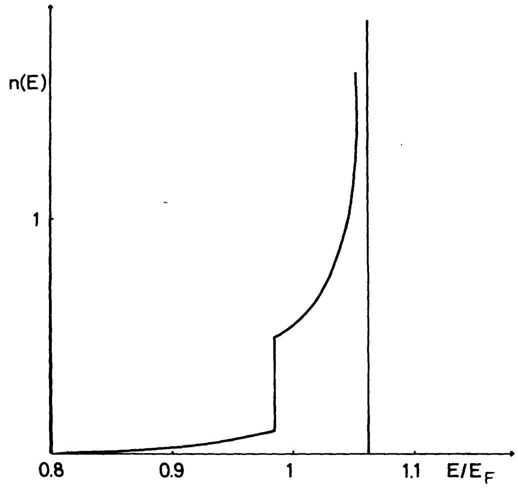

FIG. 5. Energy density of states for the antisymmetric band characterized by $\Delta=0.1$ and $E_0=2$ of Fig. 2.

value $E(0)$. When $E \geqslant E(0)$, there is a new finite contribution to $n(E)$. The density of states then increases until the energy reaches the maximum $E_{\max}$ of the surface band (see Fig. 2); near this value, $n(E)$ behaves like $(E_{\max} - E)^{-1/2}$. Figure 5 shows the behavior of the density of states of the upper band. The density of states of the lower band, when it is eventually present, is constant for E smaller than the value given by Eq. (18) and is zero otherwise.

---

[1] S. G. Davison and J. D. Levine, Solid State Phys. 25, 2 (1970).

[2] F. G. Allen and G. W. Gobelli, Phys. Rev. 127, 150 (1962).

[3] W. Mönch, Phys. Status Solidi 40, 257 (1970).

[4] V. Bortolani, C. Calandra, and A. Sghedoni, Phys. Lett. A 34, 193 (1971).

[5] D. R. Penn, Phys. Rev. 128, 2093 (1962).

[6] F. Garcia-Moliner and J. Rubio, J. Phys. C 2, 1789 (1969).

[7] See, for instance, R. A. Smith, *Wave Mechanics of Crystalline Solids* (Chapman and Hall, London, 1961).