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Symmetry criterion for surface states in solids

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A general symmetry criterion is derived for establishing the existence of surface states in solids. Two kinds of surfaces in solids are distinguished: those coinciding with symmetry planes (or symmetry centers in one dimension) and those in general positions. The symmetry criterion applies to surface states in solids terminating at symmetry planes (or symmetry centers in one dimension). A detailed discussion is given for one-dimensional crystals. The application of the symmetry criterion is demonstrated on the Kronig-Penney, nearly-free-electron, tight-binding, and Mathieu potentials. In particular, it is shown that the Maue and Shockley existence conditions for surface states follow from the general symmetry criterion.

I. INTRODUCTION

Surface states in solids were first introduced by Tamm[1] who pointed out that the disruption of the translational symmetry by the surface of the solid will, in general, lead to new states in the gaps of the energy spectrum. He called these states surface states and demonstrated their appearance on a one-dimensional Kronig-Penney model. This pioneering work was soon followed up in a number of publications. Fowler[2] and Rijanow[3] considered the appearance of Tamm surface states in model crystals limited by two surfaces. Maue[4] discussed, in detail, the formation of surface states in the free-electron approximation, and was the first one to connect the question of their existence with the sign of the Fourier components of the periodic potential. Goodwin[5] has extended Maue's results to more general potentials and considered also the appearance of surface states in the tight-binding approximation. A further contribution to surface states was made by Shockley[6] who considered the formation of surface states as a function of the interatomic distance in a finite periodic chain of atoms. He was the first one to emphasize the sensitivity of the existence condition of surface states to symmetry breaking of the potential on the boundaries of the crystal. Unlike the Tamm model[1] and the Goodwin tight-binding calculation,[5] which lead to no restrictions on the appearance of surface states in the energy gaps, the Maue[4] and the Shockley[6] models have an existence condition: in Maue's model surface states appear only in those energy gaps for which the Fourier component V of the periodic potential is negative, $V<0$; in Shockley's model band crossing is required for the appearance of surface states.

From here it followed that one can distinguish between two kinds of surface states and the first one to draw attention to their difference was Shockley.[6] He pointed out that the Maue-Shockley states are obtained for "a periodic potential without edge effects in the end cells" [Fig. 1(a) shows perfect terminations x_{v1} and x_{v3}] with the condition of "crossed bands," while the Tamm-Goodwin surface states appear when the end cell is distorted [Fig. 1(b)]. The distortion of the end cell can have two different origins. The crystal can either terminate at a general point x_{v2} (up to this point the potential is the same as in the bulk) or the potential in the end cell is different from the bulk potential and then it is not important where the termination point x_{v2}' is. The points x_{v2} and x_{v2}' are shown in Fig. 1(b).

Shockley's paper[6] caused much interest in surface states and a number of publications appeared elaborating on the two different kinds of states, and on the significance of the band crossing in the formation of surface states.[7–11] However, as time passed, the difference between the Tamm-Goodwin and the Maue-Shockley surface states, on one hand, and their existence conditions, on the other hand, have become more involved. In a review article by Davison and Levine[12] it was pointed out that the existing definitions of the Tamm and Shockley states are "hazy and sometimes misleading." It appears that this situation prevails also in recent literature and that there is no clear

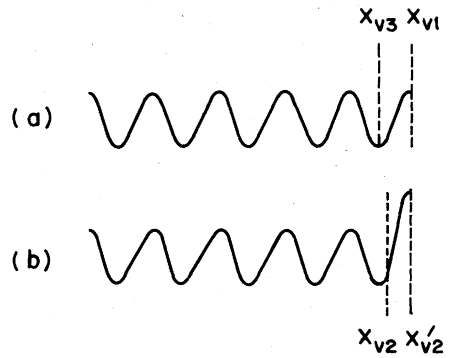

FIG. 1. Graphical description of two kinds of crystal terminations. The surface is at $x=x_v$. (a) Periodic potential with no edge effects. The surface is at symmetry centers x_{v1} or x_{v2}. Surface states in this case are of the Maue-Shockley type. (b) Periodic potential with edge effects. The latter are caused by either a nonsymmetric termination x_{v2} or by a change of the potential, and then x_{v2}' is arbitrary. In this case we have Tamm-Goodwin surface states.

distinction between the Tamm and Shockley surface states.[13–16] In particular, there seems to be no general formulation for the existence conditions of the Maue-Shockley surface states.[13]

In this paper, we derive a symmetry criterion for the existence of surface states.[17] This criterion has the meaning of a selection rule and it explains in a general framework both the Maue condition on the Fourier components in the free-electron model[4] and the band crossing in Shockley's tight-binding model.[6] It gives for the first time, a group-theoretic approach to the existence conditions of surface states. In addition, it leads also to a symmetry distinction between the Tamm and Shockley states. The idea of this symmetry distinction is very simple and can be explained by using Fig. 1. The termination points x_{v1} and x_{v3} in Fig. 1(a) are inversion centers of the crystal while the points x_{v2} or x'_{v2} [Fig. 1(b)] have no symmetry. The lack of symmetry in the end cell can be a consequence of either terminating the crystal at nonsymmetric points x_{v2}, or of changing the potential in this cell. From the point of view of symmetry, what is important is to distinguish between a surface that is on a symmetry center x_{v1} or x_{v3} (or symmetry plane in a three-dimensional crystal) and one that is on a general point x_{v2} or x'_{v2} without any symmetry. When the surface is on a symmetry center (x_{v1}, x_{v3}) one should expect that some symmetry criterion will be applicable to the corresponding surface states. These states are of the Maue-Shockley type. On the other hand, surface states which originate from a crystal with a termination at a general point, say, x_{v2} or x'_{v2} [Fig. 1(b)] should be called according to Shockley[6] the Tamm-Goodwin surface states. Naturally, no symmetry criterion applies to the latter.

In Sec. II we consider the symmetry properties of a one-dimensional crystal in the presence of a surface. It is shown that a crystal terminating at symmetry centers, e.g., x_{v1}, x_{v3} [Fig. 1(a)] preserves some symmetry of the ideal crystal. In Sec. III a symmetry criterion for the existence of surface states is derived. Section IV deals with model calculations of surface states. It is shown how the symmetry criterion applies to known models, e.g., Kronig-Penney, nearly-free-electron, tight-binding, and Mathieu potentials. Conclusions are given in Sec. V.

II. SYMMETRY PROPERTIES IN A CRYSTAL WITH A SURFACE

It is usually assumed that the crystal surface disrupts the symmetry perpendicular to the surface. Thus, in a one-dimensional crystal this assumption should mean that the introduction of a surface will disrupt the symmetry completely. However, we are going to show that the crystal with a surface preserves some symmetry of the ideal crystal. This preservation of crystal symmetry should, actually, come as no surprise if one has in mind that surface states are obtained by a matching procedure between states in the ideal crystal and states in the vacuum. Thus, in the Maue[4] and Shockley[6] models the potential is assumed to be the same as in the bulk right up to the boundary [Fig. 1(a)]. Surface states are then constructed by matching at the surface a Bloch solution in the energy gap which decays in the crystal, away from the surface, with a decaying state in the vacuum. This means that a part of the surface state is a Bloch state in the energy gap of the unperturbed crystal. Because of the matching procedure, surface states carry information of the band structure and one should expect some of the symmetry of the ideal crystal to be reflected in the surface states. This, as is shown below, is actually the case when the crystal terminates at a symmetry center, say, x_{v1} or x_{v3} in Fig. 1(a).

We show in detail how the symmetry of the ideal crystal is reflected at the surface. We shall assume that the potential is the same as in the bulk right up to the boundary and that the surface is located at a symmetry center [Fig. 1(a)]. Let x_v be the matching point between the crystal and the vacuum and let $\psi_k(x)$ and $\phi(x)$ be solutions for the surface state inside and outside the crystal correspondingly. At the matching point x_v, one demands the equality of the logarithmic derivatives of $\psi_k(x)$ and $\phi(x)$. For $\phi(x)$ this derivative at x_v is negative because for a surface state one requires that $\phi(x)$ fall off exponentially for positive x. Therefore,

$$\rho(k,x_v)=\frac{(d/dx)\psi_k(x_v)}{\psi_k(x_v)}\equiv\frac{\psi'_k(x_v)}{\psi_k(x_v)} \qquad (1)$$

has to be negative for $\psi_k(x_v)$ in the energy gap. The negativity of $\rho(k,x_v)$ is the necessary condition for the existence of surface states.[4,6,9,13] Thus, there are no surface states in an energy gap where $\rho(k,x_v)$ is positive. In what follows it is shown that the sign of $\rho(k,x_v)$ at the symmetry centers $x_{v3}=0$ and $x_{v1}=a/2$ [Fig. 1(a)] can be defined from symmetry considerations. For this we analyze the symmetry properties of $\rho(k,x_v)$ (see Ref. 9).

One distinguishes four symmetry types of bands in a one-dimensional crystal. They are shown in Fig. 2. The Bloch function of a given band, $\psi_k^{(q,l)}(x)$, can be denoted by the symmetry of the localized orbital (Wannier function) $a^{(q,l)}(x)$ of the same band according to the relation[18]

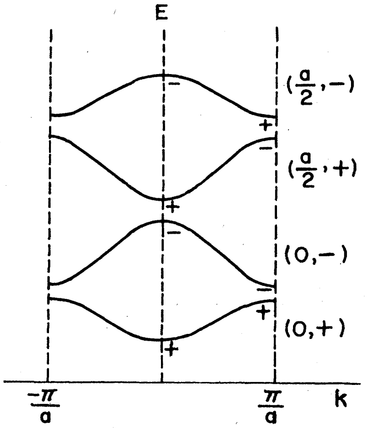

FIG. 2. Four symmetry types of energy bands. Signs on the energy bands label the parity of the Bloch functions at $k=0$ and $k=\pi/a$; the label (q,l) on the right-hand side of the bands denotes the symmetry of the band as a whole entity. Thus, $(0,+)$ means that the band center is at $q=0$ [x_{v3} in Fig. 1(a)] and the localized orbital of the band is even with respect to $q=0$.

$$\psi_k^{(q,l)}(x)=\left[\frac{a}{2\pi}\right]^{1/2}\sum_{n=-\infty}^{\infty}\exp(ikan)a^{(q,l)}(x-na)\ , \tag{2}$$

where $q=0$ or $a/2$ is a symmetry center [denoted by x_{v3} and x_{v1} correspondingly in Fig. 1(a)] and l can be plus or minus depending on whether $a(x)$ is even or odd for the inversion I with respect to the corresponding symmetry center. Thus, if the localized orbital is even with respect to the symmetry center $q=0$ [x_{v3} in Fig. 1(a)] it is denoted by $a^{(0,+)}(x)$ (Fig. 2). It is easy to check that, correspondingly, $I\psi_0^{(0,+)}(x)=\psi_0^{(0,+)}(x)$ and $I\psi_{\pi/a}^{(0,+)}(x)=\psi_{\pi/a}^{(0,+)}(x)$. It can also be checked that $\psi_k^{(0,-)}(x)$, $\psi_k^{(a/2,+)}(x)$, and $\psi_k^{(a/2,-)}(x)$ have the symmetries as shown in Fig. 2. With the notation (2) in mind, we have

$$\psi_k^{(0,\pm)}(-x)=\pm\psi_{-k}^{(0,\pm)}(x)\ , \tag{3a}$$

$$\psi_k^{(a/2,\pm)}(-x)=\pm\exp(-ika)\psi_{-k}^{(a/2,\pm)}(x)\ . \tag{3b}$$

Correspondingly, for the derivatives of the Bloch functions

$$[\psi_k^{(0,\pm)}(-x)]'=\mp[\psi_{-k}^{(0,\pm)}(x)]'\ , \tag{4a}$$

$$[\psi_k^{(a/2,\pm)}(-x)]'=\mp\exp(-ika)[\psi_{-k}^{(a/2,\pm)}(x)]'\ . \tag{4b}$$

From the definition (1) of the logarithmic derivative $\rho(k,x)$ and Eq. (2) for the Bloch functions $\psi_k^{(q,l)}(x)$ [with $a^{(q,l)}(x)$ real] it follows [for any (q,l)]

$$\rho^*(k,x)\equiv\rho^*(k_R+ik_I,x)=\rho(-k_R+ik_I,x)\ , \tag{5}$$

where k_R and k_I are the real and imaginary parts of the complex Bloch momentum k. Since by definition, $\rho(k+2\pi/a,x)=\rho(k,x)$ we have [for any (q,l)]

$$\begin{gathered}\rho^*(ik_I,x)=\rho(ik_I,x)\ ,\\ \rho^*\left[\frac{\pi}{a}+ik_I,x\right]=\rho\left[\frac{\pi}{a}+ik_I,x\right]\ .\end{gathered} \tag{6}$$

This means that $\rho(ik_I,x)$ and $\rho(\pi/a+ik_I,x)$ are both real for any x. By using Eqs. (3) and (4) one obtains [again for any (q,l)]

$$\rho(-k_R-ik_I,x)=-\rho(k_R+ik_I,-x)\ . \tag{7}$$

Combining Eqs. (5) and (7) we find for real k, $k=k_R$, and any (q,l)

$$\begin{gathered}\rho^*(k_R,0)=-\rho(k_R,0)\ ,\\ \rho^*\left[k_R,\frac{a}{2}\right]=-\rho\left[k_R,\frac{a}{2}\right]\ .\end{gathered} \tag{8}$$

This means that $\rho(k_R,0)$ and $\rho(k_R,a/2)$ are both purely imaginary. While Eqs. (3)—(7) hold for any point x in the unit cell of the crystal, Eq. (8) is written for the symmetry centers $x_v=0$ and $x_v=a/2$ only. For the latter, Eqs. (3)—(8) lead to information about $\rho(k,x_v)$ which is of much importance in establishing the existence conditions for surface states. First of all, from Eqs. (3a) and (3b) we obtain the zeros of the Bloch functions $\psi_k(x)$ and of their derivatives $\psi'_k(x)$. They are listed in the upper half of Table I, and these are all possible zeros of $\psi_k(x)$ and $\psi'_k(x)$ that follow from the symmetry of the crystal. By using these zeros and the definition (1) we find the lower part of Table I which lists the zeros and infinities of $\rho(k,x_v)$ at different band edges k and symmetry centers x_v in the Brillouin zone and the Wigner-Seitz cell correspondingly. We would like to point out that these are all zeros and infinities of $\rho(k,x_v)$ that follow from the symmetry of the Bloch functions. In particular, $\rho(k,x_v)$ has no zeros or infinities at complex values of k, a result which is of much importance in the derivation of the existence conditions for surface states. Thus, assume that at some symmetry center x_v and at some k' in the energy gap ($k'=ik_I$ or $k'=\pi/a+ik_I$ with $k_I\neq 0$) $\rho(k',x_v)>0$ [according to Eq. (6), at these values of k', ρ is real and we can therefore assume that it is positive]. As long as k' stays complex, the sign of $\rho(k',x_v)$ cannot change because it does not assume zero or infinity at complex k' [at the edges of the energy band, $\rho(k',x_v)$ can change sign by going through 0 or ∞]. This sign constancy of ρ in the energy gap will be used in the next section in establishing the symmetry criterion for surface states.

TABLE I. In the upper half it is indicated at which values of (k,x_v), the $\psi_k(x_v)$, and $\psi'_k(x_v)$ vanish. In the lower half the values of $\rho(k,x_v)$ are listed at different symmetry centers and edges of the energy bands.

(k,x_v) (q,l)	$(0,0)$	$(0,a/2)$	$(\pi/a,0)$	$(\pi/a,a/2)$
$(0,+)$	$\psi'=0$	$\psi'=0$	$\psi'=0$	$\psi=0$
$(0,-)$	$\psi=0$	$\psi=0$	$\psi=0$	$\psi'=0$
$(a/2,+)$	$\psi'=0$	$\psi'=0$	$\psi=0$	$\psi'=0$
$(a/2,-)$	$\psi=0$	$\psi=0$	$\psi'=0$	$\psi=0$
$(0,+)$	$\rho=0$	$\rho=0$	$\rho=0$	$\rho=\infty$
$(0,-)$	$\rho=\infty$	$\rho=\infty$	$\rho=\infty$	$\rho=0$
$(a/2,+)$	$\rho=0$	$\rho=0$	$\rho=\infty$	$\rho=0$
$(a/2,-)$	$\rho=\infty$	$\rho=\infty$	$\rho=0$	$\rho=\infty$

III. SYMMETRY CRITERION FOR SURFACE STATES

In the preceding section we have shown that ρ for values of k in the energy gap preserves its sign. Now we will show that $\rho(k,x_v)$ can change sign when x_v is kept constant at a given symmetry center and when k changes from one energy gap to another one by traversing an energy band. Moreover, it will be shown that the change of sign of $\rho(k,x_v)$ is fully controlled by the symmetry of the energy band that is being traversed. Thus, if an energy band with a given symmetry (q,l) [see Fig. 3(b)] separates two gaps $E_g^{(1)}$ and $E_g^{(2)}$, then, as will be shown below, if the sign of $\rho(k,x_v)$ is known in one of these gaps, say, $E_g^{(1)}$, the symmetry (q,l) of the band fully determines the sign of ρ in the gap $E_g^{(2)}$.

Consider, for example, the band $(0,+)$ of Fig. 2 and assume that ρ at energies below this band is positive $\rho(-i\beta,0)>0$. We choose the imaginary part to be $-i\beta$ so that the Bloch function inside the crystal falls off for negative x [see Fig. 1(a)]. The choice of ρ to be positive at all energies below the band $(0,+)$ is consistent with the proof in the preceding section of the sign constancy of ρ at imaginary k. The question we ask is what is the sign of

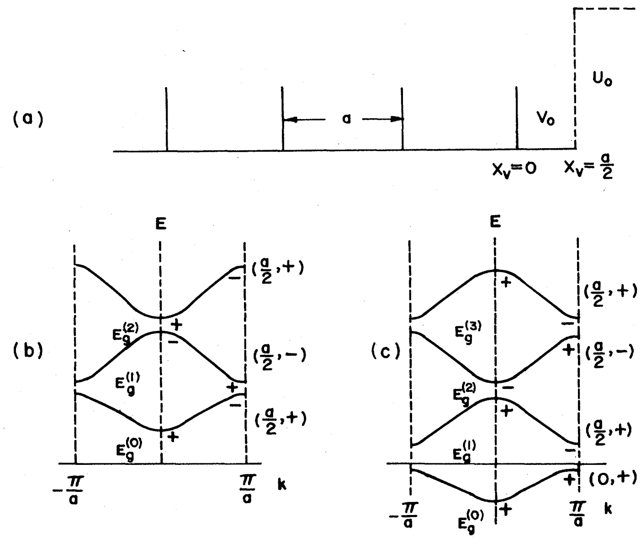

FIG. 3. Kronig-Penney model. (a) Periodic potential of height V_0 with a surface potential U_0. $x_v=0$ and $x_v=a/2$ are symmetry centers (a is the lattice constant). (b) Symmetry of the energy bands for $V_0>0$. (q,l) on the right-hand side is as in Fig. 2. $E_g^{(n)}$ number the energy gaps. (c) As in (b), but for $V_0<0$.

ρ in the gap after going through the band $(0,+)$, or what is the sign of $\rho(\pi/a-i\beta,0)$? From Table I we know that $\rho(0,0)=\rho(\pi/a,0)=0$. From Eq. (8) it is also known that for real k, $\rho(k,0)$ is purely imaginary while $\rho(-i\beta,0)$ and $\rho(\pi/a-i\beta,0)$ are real [see Eq. (6)]. For small k both $\rho(k,0)$ and $\rho(\pi/a-k,0)$ are analytic in k.[19] From the assumption $\rho(-i\beta,0)>0$ it follows that for real k, $\rho(k,0)\sim ik$ (because for $k=-i\beta$, ρ has to be positive). Since $\rho(k,0)$ has no zeros on the real axis (with the exception of $k=0$ and $k=\pi/a$) this means that $\rho(k,0)$ cannot change sign. We therefore have $\rho(\pi/a-k,0)\sim ik$. From here it follows that $\rho(\pi/a-i\beta,0)\sim-\beta<0$. This means that $\rho(k,0)$ changes sign when traversing the band with the symmetry $(0,+)$.

The situation is different for $\rho(k,a/2)$ when traversing the same band $(0,+)$. Here, since $\rho(\pi/a,a/2)=\infty$ (see Table I) we have that $\rho(\pi/a-k,a/2)\sim i/k$, and therefore $\rho(\pi/a-i\beta)\sim 1/\beta>0$. The conclusion is that there is no change of sign for $\rho(k,a/2)$ when traversing the band $(0,+)$. In a similar manner, by using the information of Table I, one finds the sign changes of $\rho(k,0)$ and $\rho(k,a/2)$ when traversing an energy band that belongs to one of the remaining three symmetry types. These sign changes are summarized in Table II. As will soon be shown they can be used for establishing a symmetry criterion for the existence of surface states.

Before discussing Table II we first prove a relation connecting $\rho(k,0)$ with $\rho(k,a/2)$. For this we use the Wronskian[20]

$$W(x)=g(x)u'(x)-g'(x)u(x) \tag{9}$$

for the solutions

$$g(x)=\psi_k(x)+\psi_k(-x),\quad u(x)=\psi_k(x)-\psi_k(-x) \tag{10}$$

TABLE II. Sign changes of $\rho(k,x_v)$ when traversing a band with a given symmetry (q,l).

(q,l) $\frac{\rho(-i\beta,x_v)}{\rho(\pi/a-i\beta,0)}$	$(0,+)$	$(0,-)$	$(a/2,+)$	$(a/2,-)$
$\frac{\rho(-i\beta,0)}{\rho(\pi/a-i\beta,0)}$	−	−	+	+
$\frac{\rho(-i\beta,a/2)}{\rho(\pi/a-i\beta,a/2)}$	+	+	−	−

of the one-dimensional Schrödinger equation. $g(x)$ is even, while $u(x)$ is odd. Since $W(x)$ does not depend on x we have $W(0)=W(a/2)$ and from (9) and (10) it follows

$$\rho(k,0)=\frac{\psi_k^2(a/2)}{\psi_k^2(0)}\rho\left[k,\frac{a}{2}\right]\exp(-ika)\ . \tag{11}$$

For $k=-i\beta$ and $k=\pi/a-i\beta$, $\psi_k(x)$ is real, and the squares of the wave functions in (11) are positive. The factor $\exp(-ika)$ is positive at $k=-i\beta$ and negative at $k=\pi/a-i\beta$, and from (11) it follows

$$\operatorname{sgn}[\rho(-i\beta,0)]=\operatorname{sgn}\left[\rho\left[-i\beta,\frac{a}{2}\right]\right]\ , \tag{12}$$

$$\operatorname{sgn}\left[\rho\left[\frac{\pi}{a}-i\beta,0\right]\right]=-\operatorname{sgn}\left[\rho\left[\frac{\pi}{a}-i\beta,\frac{a}{2}\right]\right]\ . \tag{13}$$

These relations contain important information for determining the existence of surface states. As was already pointed out [see Eq. (1)], only if $\rho(k,x_v)$ is negative can surface states exist. From Eq. (12) it therefore follows that if the band edge is $k=0$ and there are no surface states at one symmetry center of the crystal, say, $x_v=0$, there are no surface states at the other center, $x_v=a/2$. The situation is different for a band edge at $k=\pi/a$. In this case, as it follows from Eq. (13), if surface states are forbidden at one of the symmetry centers, say, $x_v=0$, they are allowed at the other center, $x_v=a/2$, and vice versa. Equations (12) and (13) can therefore be useful in establishing existence conditions for surface states.

We now discuss the results of Table II. This table contains the ratios of the values of ρ in two adjacent gaps that are separated by a band of given symmetry. Thus, by assuming that $\rho(-i\beta,0)$ below the band $(0,+)$ (see Fig. 2) is positive, we find from Table II that, in the gap above the band $(0,+)$, $\rho(\pi/a-i\beta,0)<0$. Since the gap below the band $(0,+)$ has its edge at $k=0$, it follows from (12) that also $\rho(-i\beta,a/2)>0$. From Table II we find that $\rho(\pi/a-i\beta,a/2)>0$ in the gap above the band $(0,+)$. The edge of the gap above $(0,+)$ is at $k=\pi/a$ and the signs of ρ in this gap, $\rho(\pi/a-i\beta,0)<0$ and $\rho(\pi/a-i\beta,a/2)>0$ are in agreement with Eq. (13). Having the signs of ρ above the band $(0,+)$ we can continue using Table II and find the signs of $\rho(-i\beta,0)$ and $\rho(-i\beta,a/2)$ above the band $(0,-)$. Thus, $\rho(-i\beta,0)>0$ and $\rho(-i\beta,a/2)>0$. Since the edge of this gap is at

$k=0$, it is in agreement with Eq. (12) to have the same sign for ρ at $x_v=0$ and at $x_v=a/2$. Similarly, by using the information about the sign switching of Table II one can derive the sign of ρ in any gap of the energy spectrum, provided the sign of ρ is known in one gap, e.g., in the gap below the band $(0,+)$. In general, this latter information depends on the explicit form of the potential. However, as is shown in the next section, $\rho(-i\beta,0)$ and $\rho(-i\beta,a/2)$ are positive in the lowest gap for the surface states of Tamm,[1] the nearly-free-electron model of Maue,[4] the Shockley model,[6] and the Mathieu potential.[12] Assuming this to be a general feature of one-dimensional crystals one can then find from Table II the absolute signs of $\rho(k,0)$ and $\rho(k,a/2)$ in any gap of the energy spectrum.

The information contained in Table II can be summarized in the following symmetry criterion: When traversing a band of symmetry (q,l) $(q=0,a/2)$, $\rho(k,x_v)$ $(x_v=0,a/2)$ preserves its sign for $x_v\neq q$ and changes sign for $x_v=q$. In the next section we show how this symmetry criterion applies to different models of surface states.

IV. MODEL CALCULATIONS OF SURFACE STATES

The existence of surface states for a semi-infinite crystal is determined by the sign of the quantity $\rho(k,x_v)$ in Eq. (1). Thus, only if $\rho(k,x_v)<0$ for k in the energy gap can there be surface states in this gap. In the preceding section it was shown that the change of sign of $\rho(k,x_v)$, for x_v fixed, when traversing an energy band is fully determined by the symmetry of this band. If in addition one knows the sign of ρ in one gap, say, below the lowest energy band, then the symmetry structure of the energy bands fixes completely the absolute sign of ρ.

In this section we find the signs of $\rho(k,x_v)$ in direct model calculations of surface states and compare them with the corresponding signs of $\rho(k,x_v)$ that follow from our symmetry criterion. In particular, we will show how the existence conditions for surface states of Maue[4] and Shockley[6] follow from the symmetry criterion. The following models will be analyzed: (1) Tamm's Kronig-Penney model, (2) Maue's nearly-free-electron calculation, (3) Shockley's tight-binding approximation, and (4) the Mathieu potential.

A. Kronig-Penney model

Tamm[1] was the first one to predict a surface state in solids. His calculations were carried out on the Kronig-Penney potential with $V_0>0$ [see Fig. 3(a)]. A very good discussion of the Bloch problem for this model is given in Ref. 20. Tamm considered the surface at $x_v=0$ (Fig. 3) where the actual potential is discontinuous and in order to avoid the discontinuity he removed the δ function at $x_v=0$. Shockley[6] discussed Tamm's choice of surface in detail and we shall return to this point later. In our discussion we shall choose the surface at $x_v=a/2$ where there is no discontinuity and we therefore expect our symmetry criterion to apply to it. As can be shown, the wave function $\psi_k(x)$ in the crystal for $0\leq x\leq a/2$ is[12]

$$\psi_k(x)=A[\exp(ika)\sin\alpha x-\sin\alpha(x-a)]\ , \tag{14}$$

where A is a constant and $\alpha^2=2mE/h^2$, with E being the energy. From the expression for $\psi_k(x)$ and definition (1), we have

$$\rho\left[k,\frac{a}{2}\right]=i\alpha\cot\frac{\alpha a}{2}\tan\frac{ka}{2}\ . \tag{15}$$

We analyze the sign of this expression in the energy gaps of the spectrum. We shall denote the lowest energy gap (below the lowest band) by $E_g^{(0)}$. Correspondingly, $E_g^{(1)},E_g^{(2)},\ldots$ are the gaps above the first energy band, the second, and so on [see Fig. 3(b)]. For energies in the gap the quasimomentum k is complex and it can assume the value $k=-i\beta$ and $k=\pi/a-i\beta$ depending on whether the edge of the energy band is at $k=0$ or $k=\pi/a$ (the choice of the imaginary part $-i\beta$ with the negative sign is dictated by the fact that the crystal extends to the left [see Fig. 3(a)] and this leads to the falloff of the Bloch function in the crystal away from the surface). $\tan(ka/2)$ in the expression (15) for these values of k becomes

$$\tan\left[-\frac{i\beta a}{2}\right]=-i\tanh\frac{\beta a}{2}\ ,$$
$$\tan\left[\frac{\pi}{a}-\frac{i\beta a}{2}\right]=-i\coth\frac{\beta a}{2}\ . \tag{16}$$

The sign of $\cot(\alpha a/2)$ in the expression (15) varies from gap to gap and is as follows:[20]

$$\operatorname{sgn}\left[\cot\frac{\alpha a}{2}\right]=(-1)^n \ \text{ for } n\pi<\alpha a<(n+1)\pi\ , \tag{17}$$

where the integer n labels the number of the energy gap $E_g^{(n)}$ in the spectrum. By using Eqs. (16) and (17) we find the sign of the left-hand side in the expression (15) for $V_0>0$:

$$\operatorname{sgn}\left[i\alpha\cot\alpha\tan\frac{ka}{2}\right]=\operatorname{sgn}[(-1)^n],\quad n=0,1,2,\ldots\ . \tag{18}$$

This means that no surface states can exist in the Kronig-Penney model with the surface at $x_v=a/2$ in the even-numbered energy gaps $E_g^{(2n)}$.

Having found the existence of surface states via the direct calculation of the sign of $\rho(k,x_v)$, it is instructive to compare these results with the signs of $\rho(k,x_v)$ that follow from applying the symmetry criterion. For its application we need the symmetry of the energy bands. We denote the bands by E_{mk} and correspondingly, the Bloch functions by ψ_{mk}. The following results are known for the bottoms and tops of the energy bands in the Kronig-Penney model[20] (for $V_0>0$): Bottoms of $E_{2l+1\,k}$ are at

$$k=0 \quad \text{for } 2l\pi < \alpha a < (2l+1)\pi \;,$$

tops of $E_{2l+1\,k}$ are at

$$k=\frac{\pi}{a} \quad \text{for } \alpha a = (2l+1)\pi \;,$$

bottoms of $E_{2l\,k}$ are at (19)

$$k=\frac{\pi}{a} \quad \text{for } (2l-1)\pi < \alpha a < 2l\pi \;,$$

and tops of $E_{2l+1\,k}$ are at

$$k=0 \quad \text{for } \alpha a = 2l\pi \;.$$

From these results and the expression (14) for the wave function we can find the parity of the latter at the symmetry points $k=0$ and $k=\pi/a$ in the Brillouin zone. We use the fact that an odd Bloch function vanishes at $x=0$ while an even Bloch function does not. The parity of the Bloch functions for the Kronig-Penney model with $V_0>0$ is summarized in Fig. 3(b) showing that it alternates from edge to edge all the way to infinity. In the notation of band symmetry [Eq. (2)], the lowest band is $(a/2,+)$ the next band is $(a/2,-)$, the following band is $(a/2,+)$, and so on. In applying the symmetry criterion, the additional information we need is the sign of $\rho(k,x_v)$ in one energy gap, say, in $E_g^{(0)}$. From (15) and (18) for $n=0$ we have $\rho^{(0)}(-i\beta,a/2)>0$ in $E_g^{(0)}$. According to the symmetry criterion of the preceding section (Table II), $\rho^{(1)}(\pi/a-i\beta,a/2)<0$, $\rho^{(2)}(-i\beta,a/2)>0$, and so on. The sign alteration of ρ when going from one energy gap to the next is a consequence of the fact that all the bands have their symmetry centers at $q=a/2$ while the surface is at the same center, $x_v=a/2$. From the symmetry criterion it follows that when traversing such a band $(q=x_v)$ ρ will change sign and since in $E_g^{(0)}$, $\rho(-i\beta,a/2)>0$, the symmetry criterion leads to the same results as from direct calculations [see Eqs. (15) and (18)].

As was already pointed out, in his original paper, Tamm[1] placed the surface at $x_v=0$ and matched the wave function and its derivative assuming a finite step potential U_0 and no $\delta(x)$ function of this point [see Fig. 3(a)]. Such an assumption is equivalent to changing the periodic potential at the boundary, as was pointed out by Shockley.[6] The removal of $\delta(x)$ at $x_v=0$ makes the potential nonsingular and enables the matching of both the function and its derivative at this point (for a δ function there is a discontinuity in the derivative[12,20]). However, this removal changes the periodic potential at $x_v=0$ and the surface is no longer at a symmetry center of the crystal. According to Shockley, surface states for a surface not at a symmetry center of the crystal should be called Tamm-Goodwin states. As was shown by Tamm,[1] these kind of surface states can appear in any energy gap and there is no existence criterion for them.

Unlike $x_v=0$, the point $x_v=a/2$ is a symmetry center in the Kronig-Penney model and Eq. (18) shows that surface states cannot appear in even-numbered gaps, e.g., $n=0,2,4,\ldots$. As was shown above, Eq. (18) is a consequence of the symmetry structure of the energy bands in the Kronig-Penney model.

A similar discussion can be carried out for $V_0<0$. Without going into details we shall just summarize the results. The symmetry of the bands is given in Fig. 3(c). It differs from the band symmetry for $V_0>0$ [Fig. 3(b)] that in the case of $V_0<0$, the energy spectrum extends to negative energies and the lowest band has the symmetry $(0,+)$. The symmetry of the other bands for $V_0<0$ [Fig. 3(c)] coincides with the case of $V_0>0$. By applying the symmetry criterion to the band structure in Fig. 3(c) we find that no surface state can appear in the following energy gaps for $V_0<0$ $(x_v=a/2)$:

$$E_g^{(0)} \text{ and } E_g^{2n+1}, \quad n=0,1,2,\ldots \;. \tag{18$'$}$$

Unlike the case $V_0>0$ where surface states are forbidden in even-numbered gaps [Eq. (18)], in the case $V_0<0$ there are no surface states in the Kronig-Penney model in the lowest gap $E^{(0)}$ and in all odd-numbered gaps [Eq. (18′)].

B. Nearly-free-electron model

When the periodic potential $V(x)$ is weak, one can take it into account in the framework of perturbation theory. Such a model for surface states was considered in detail by Maue,[4] who also was the first one to establish for them an existence condition. We show in this section how the latter can be obtained from the symmetry criterion for surface states. The summary of Maue's results is as follows. For a periodic potential of the form

$$V(x)=V_l\left[\exp\left[i\frac{2\pi}{a}xl\right]+\exp\left[-i\frac{2\pi}{a}xl\right]\right]+V_0 \;, \tag{20}$$

one looks for a Bloch function,

$$\psi_k(x)=\exp(ikx)\left[\alpha_l\exp\left[i\frac{\pi}{a}lx\right]+\beta_l\exp\left[-i\frac{\pi}{a}lx\right]\right] \;, \tag{21}$$

where V_l denotes the lth Fourier component of the periodic potential, V_0 relates the potential of the solid to the vacuum level, and α_l,β_l are unknown coefficients. Perturbation theory gives for the energy E and for the coefficients α_l and β_l the results (we shall restrict ourselves to $l=1$)[4]

$$E_{1,2}=\frac{\hbar^2}{2m}\left\{k^2+\left[\frac{\pi}{a}\right]^2\mp 2\left[k^2\left[\frac{\pi}{a}\right]^2+\frac{m^2}{\hbar^4}V_1^2\right]^{1/2}\right\} + V_0 \;, \tag{22}$$

$$\left[\frac{\beta_1}{\alpha_1}\right]_{1,2}=\frac{\hbar^2}{mV_l}\left\{-k\frac{\pi}{a}\mp\left[k^2\left[\frac{\pi}{a}\right]^2+\frac{m^2}{\hbar^4}V_1^2\right]^{1/2}\right\} , \tag{23}$$

where the indices 1 and 2 are for the lower and upper bands correspondingly. By assuming, as in Figs. 1(a) and 3(a), that the crystal extends for negative values of x and that the vacuum is for $x>0$, k is set at $k=-i\beta$ $(\beta>0)$, and the Bloch function (21) can be written $[\alpha_1=\exp(i\delta)$, $\beta_1=\exp(-i\delta)]$

$$\psi_{-i\beta}(x)=A\exp(\beta x)\cos\left[\frac{\pi}{a}x+\delta\right], \tag{24}$$

where A is a constant and

$$\sin 2\delta=-\frac{\hbar^2}{2mV_l}\frac{2\pi}{a}\beta. \tag{25}$$

By matching (24) (and its derivative) to the wave function in the vacuum (the potential of the vacuum is zero),

$$\sim\exp\{-[(2m/\hbar^2)\,|E|\,]^{1/2}x\},$$

one obtains Maue's relation for surface states:[4]

$$\frac{\pi}{a}\tan\left[\frac{\pi}{a}x_v+\delta\right]=\left[\frac{2m}{\hbar^2}|E|\right]^{1/2}+\beta, \tag{26}$$

where x_v is the position of the surface. In the original work only $x_v=0$ was considered. In this case (26) becomes

$$\frac{\pi}{a}\tan\delta=\left[\frac{2m}{\hbar^2}|E|\right]^{1/2}+\beta. \tag{26$'$}$$

Since the right-hand side of (26′) is positive it is clear that this relation can be satisfied only when $V_1<0$, because from (25) it follows

$$-\frac{\pi}{2}<\delta<0 \text{ for } V_1>0,$$
$$0<\delta<\frac{\pi}{2} \text{ for } V_1<0. \tag{27}$$

Thus, $V_1<0$ is Maue's existence condition for surface states at $x_v=0$ in the nearly-free-electron approximation.

When $x_v=a/2$, Eq. (26) becomes

$$-\frac{\pi}{a}\cot\delta=\left[\frac{2m}{\hbar^2}|E|\right]^{1/2}+\beta. \tag{26$''$}$$

With Eq. (27) in mind it is clear that Eq. (26″) can be satisfied only when $V_1>0$. This means that for $x_v=a/2$ Maue's existence condition is $V_1>0$.

It is easy to show how Maue's existence condition for surface states follows directly from our symmetry criterion. From Eqs. (21) and (23) we find the Bloch function at the top of the first band:

$$\psi_{1\,\pi/a}(x)=A\sin\frac{\pi}{a}x \text{ for } V_1>0,$$
$$\psi_{1\,\pi/a}(x)=A\cos\frac{\pi}{a}x \text{ for } V_1<0, \tag{28}$$

where A is a constant. At the bottom of the first band, the Bloch function is a constant and therefor of even parity. This means that the first band in the nearly-free-electron approximation is

$$\left[\frac{a}{2},+\right] \text{ for } V_1>0$$

[the first band in Fig.3(b)], (29)

$$(0,+) \text{ for } V_1<0$$

(the first band in Fig. 2). In the gap $E_g^{(0)}$ (below the first band) both $\rho^{(0)}(-i\beta,0)$ and $\rho^{(0)}(-i\beta,a/2)$ are positive (the superscript 0 denotes the gap $E_g^{(0)}$). This follows from the expression of the Bloch function $\exp(qx)$ in $E_g^{(0)}$. We can now apply the symmetry criterion: when traversing the band $(a/2,+)$, $\rho(k,0)$ keeps its sign while $\rho(k,a/2)$ changes sign; for the band $(0,+)$ it is the other way around and $\rho(k,0)$ changes sign, while $\rho(k,a/2)$ remains positive. The application of the symmetry criterion leads to Maue's existence condition for surface states in the nearly-free-electron approximation in the first gap $E_g^{(1)}$ of the energy spectrum: at $x_v=0$, no surface states for

$$V_1>0,$$

and at $x_v=a/2$, no surface states for (30)

$$V_1<0.$$

C. Tight-binding approximation

Shockley[6] used a tight-binding model for calculating surface states. In this model, the Bloch function $\psi_k(x)$ can be expressed in the form (2) where $a^{(q,l)}(x)$ is an atomic orbital. Shockley considered in detail an s orbital, $a^{(0,+)}(x)$, and a p orbital, $a^{(0,-)}(x)$, with respect to the symmetry center at the origin, $q=0$. The energy bands corresponding to these two orbitals are plotted in Fig. 2 (the first two bands). By a direct calculation, Shockley showed that as long as the lattice parameter is sufficiently large so that the s and p bands do not cross, there can be no surface states in the gap between these two bands. In Shockley's model $x_v=a/2$ and his result can be easily reproduced from our symmetry criterion. The only additional information we need to know is what is the sign of $\rho(-i\beta,a/2)$ below the s band. For well-separated orbitals we have from Eq. (2) in the interval $a/2\le x\le a/2$

$$\psi_k^{(0,+)}(x)\approx\left[\frac{a}{2\pi}\right]^{1/2}[a_s^{(0,+)}(x)+\exp(ika)a_s^{(0,+)}(x-a)$$
$$+\exp(-ika)a_s^{(0,+)}(x+a)]. \tag{31}$$

By assuming an exponential falloff for $a_s^{(0,+)}(x)$ and by using definition (1), we have

$$\rho(-i\beta,0)>0 \text{ and } \rho\left[-i\beta,\frac{a}{2}\right]>0. \tag{32}$$

With this information at hand we can now apply the symmetry criterion for finding the sign of ρ above the s band. By traversing the s band, $(0,+)$, $\rho^{(0,+)}(-i\beta,a/2)$ does not change sign because $q\neq x_v$, and therefore $\rho(\pi/a-i\beta,a/2)>0$. This means that no surface states can appear in the gap above the s band which agrees with Shockley's existence criterion. When the atoms are brought together, the s and p bands $[(0,+)$ and $(0,-)$ in Fig. 2] might cross and the lowest band will assume the symmetry $(a/2,+)$ (Fig. 2) corresponding to an even Bloch function at the bottom and an odd Bloch function at the top of the band. When such a band is traversed by $\rho(k,a/2)$ it changes sign according to the symmetry criterion (because now $x_v=q$) and surface states are no longer forbidden. It is clear that if one chooses the surface at $x_v=0$ in the Shockley model then surface states are forbidden above the s band $[(0,+)$ in Fig. 2] because for this configuration, $x_v=q$ and ρ changes sign when going through the $(0,+)$ band. Therefore, we see that what actually counts in the symmetry criterion is not whether or not bands have crossed, but rather what the explicit symmetry of the band is, and where the surface is placed. In fact, for $x_v=0$, in the Shockley model, surface states would disappear after the s and p bands have crossed. Band crossing in the Shockley model is a means of changing the symmetry of the band: Thus, if the s band, before crossing with the p band, had the symmetry $(0,+)$, it changes its symmetry to $(a/2,+)$ after the crossing takes place. This symmetry change leads to a change of sign in ρ and, correspondingly, removes the selection rule for the surface states.

D. Mathieu potential

One of the analytically solvable examples of the Schrödinger equation with periodic potentials is the Mathieu potential. For surface states, this problem was analyzed in detail by Levine.[21] Unlike the Kronig-Penney model, which is also analytically solvable, the Mathieu potential is everywhere continuous and the existence of surface states can be considered for surfaces at both symmetry centers $x_v=0$ and $x_v=a/2$ [in the Kronig-Penney model, the potential is singular at $x_v=0$, the derivative of the Bloch function at this point is discontinuous, and $\rho(k,x_v)$ is not defined at $x_v=0$]. In applying the symmetry criterion to the existence of surface states we heed the symmetry of the energy bands and the sign of ρ in one energy gap, say, $E_g^{(0)}$. The potential in the Mathieu model is given by Eq. (20) with $l=1$. This case was discussed in Sec. IV B in the perturbation approximation. Here, this problem is discussed without any approximation. The band symmetry is well known for the Mathieu potential and for $V_1>0$ it is given in Ref. 21 [see Fig. 4(a)]. From the point of view of symmetry it coincides for $V_1>0$ with the symmetry structure of the energy spectrum for the Kronig-Penney model [see Figs. 3(b) and 4(a)]. For $V_1<0$ it can be shown to coincide with the sequence $(0,+)$, $(0,-)$, $(0,+)$, and so on [see Fig. 4(b)]. As to the sign of $\rho(-i\beta,0)$ in $E_g^{(0)}$, the lowest energy gap, it is found explicitly in Ref. 21 and it is positive: $\rho(-i\beta,0)>0$. The same also holds at $x_v=a/2$: $\rho(-i\beta,a/2)>0$ [from Eq. (12)]. We first apply the symmetry criterion to the case $V_1>0$. Since the energy bands are centered at $q=a/2$ [Fig. 4(a)], $\rho(k,0)$ conserves sign according to the symmetry criterion $(q\neq x_v)$ when traversing an energy band, while $\rho(k,a/2)$ changes sign $(q=x_v)$. The signs of ρ for different energy gaps in the Mathieu potential are summarized in Table III (for $V_1>0$). Thus, no surface states can appear for a surface at $x_v=0$, while for $x_v=a/2$ surface states are forbidden in the even-numbered gaps. These results are well known from Ref. 21 where they were obtained by a direct calculation of the matching conditions. Here, we obtain them from the general symmetry criterion when applied to the Mathieu potential with $V_1>0$. It should be pointed out that the possible appearance of surface states in the odd-numbered gaps has nothing to do with band crossing. In fact, no band crossing is at all possible in the Mathieu potential.[21]

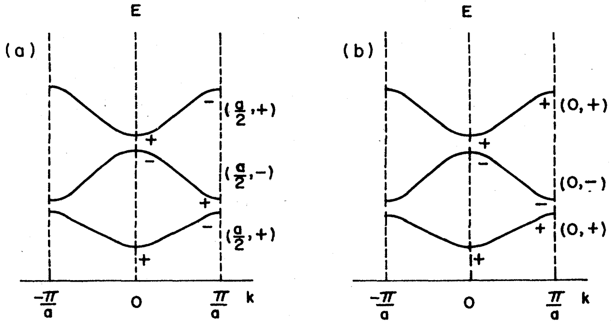

FIG. 4. Symmetry of the energy bands in the Mathieu potential. For notations see Fig. 2. (a) For $V_0>0$; (b) for $V_0<0$.

For $V_1<0$ the band symmetry is given in Fig. 4(b). The same arguments as above show that in this case, no surface states are allowed for $x_v=a/2$ and that they are also forbidden in the even-numbered gaps for $x_v=0$. In other words, for $V_1<0$, $x_v=0$ and $x_v=a/2$ exchange places in comparison with the case of $V_1>0$. See the results for the signs of ρ in Table III for $V_1<0$.

The analysis has shown that there is no difference, from the point of view of symmetry, between the two symmetry centers $x_v=0$ and $x_v=a/2$. At $x_v=0$ there are no surface states for $V_1>0$, while for $x_v=a/2$, no surface states can exist for $V_1<0$. Surface states can appear in the odd-numbered gaps for $V_1>0$ at $x_v=a/2$ and for $V_1<0$ at $x_v=0$ (see Table III). In Ref. 21 the points $x_v=0$ and $x_v=a/2$ are considered as distinct, and Shockley states are assigned to $x_v=0$ while at $x_v=a/2$ it is claimed that "the potential is terminated in a highly asymmetric manner" and that one would expect to see Tamm states at $x_v=a/2$. There does not seem to be any justification for such a distinction between $x_v=0$ and $x_v=a/2$. Both points, $x_v=0$ and $x_v=a/2$, are symmetry

TABLE III. Summary of the signs of ρ for the Mathieu potential. The superscript in ρ denotes the number of the gap. x_v is a symmetry center.

ρ \ x_v	$V_1>0$		$V_1<0$	
	$x_v=0$	$x_v=a/2$	$x_v=0$	$x_v=a/2$
$\rho^{(2n)}$	+	+	+	+
$\rho^{(2n+1)}$	+	−	−	+

centers of the one-dimensional crystal, and from the point of view of symmetry they are *indistinguishable*. At both points, symmetry arguments apply and surface states are equally forbidden by the symmetry criterion. Following Shockley[6] and the discussion in the Introduction for different crystal terminations, the surface states for both symmetry centers $x_v=0$ or $x_v=a/2$ are of the Maue-Shockley type. We do not see any justification for assigning Tamm states to the point $x_v=a/2$ and Shockley states to the point $x_v=0$ as was done in Ref. 21. In fact, the Maue model that was discussed in Sec. IV B is nothing else but a perturbation approach to the Mathieu potential. Thus, Maue's existence conditions are identical with the ones summarized in Table III for $\rho^{(1)}$, in the gap $E_g^{(1)}$.

V. CONCLUSIONS

We have shown that despite the fact that a surface disrupts the translational symmetry of the crystal, a symmetry criterion can be derived for the existence of surface states. The concepts of symmetry centers and of symmetries of energy bands as whole entities are used in deriving this criterion. A distinction is made between surfaces at symmetry centers[18,22] and those which appear at general points in the crystal. Maue-Shockley states are associated with the former types of surfaces while Tamm-Goodwin states belong to the latter type. The symmetry criterion applies to Maue-Shockley states. Maue's[4] existence criterion is explained in the framework of the symmetry criterion. Band crossing in the Shockley model[6] is interpreted as a means of changing the symmetry of an energy band. The symmetry criterion shows that what actually counts is the symmetry of bands as whole entities and not whether or not bands cross. The symmetry criterion is applied to four one-dimensional models: Kronig-Penney, nearly-free-electron and tight-binding models, and the Mathieu potential.

We would like to point out that the results of Tables I and II can directly be carried over to a wide class of real three-dimensional crystals. The relevant information needed for deriving the symmetry criterion is the zeros of the Bloch functions at different symmetry planes in the crystal and at different symmetry points in the Brillouin zone (see upper half of Table I). For an energy band with a given symmetry[18] it is very easy to find the zeros of the Bloch functions. Thus, for an s band $(\mathbf{q},+)$ or a p band $(\mathbf{q},-)$ with $\mathbf{q}=\mathbf{0}$ or $\mathbf{q}=(a/2,0,0)$ in a cubic crystal we obtain the same results as in Table I with the difference that now ψ and ρ are functions of $\mathbf{k}$ and $\mathbf{r}_v$: $k=0$ and $k=\pi/a$ should be replaced by $\mathbf{k}=\mathbf{0}$ and $\mathbf{k}=(\pi/a,0,0)$, while instead of $x_v=0$ and $x_v=a/2$ the vectors $\mathbf{r}_v=(0,y,z)$ and $\mathbf{r}_v=(a/2,y,z)$ will appear with arbitrary y and z. The sign changes of Table II will then hold for the corresponding functions $\rho(\mathbf{k},\mathbf{r}_v)$. The information of Tables I and II is therefore applicable to three-dimensional crystals. However, care must be taken when dealing with three dimensions. The reason for this is that in three dimensions we have many more symmetry points in the Brillouin zone that in one dimension and it might happen that some of them are not invariant under the reflection in a particular symmetry plane of the crystal. This, for example, is the case for the $X=(2\pi/a,0,0)$ point in the Brillouin zone for a zinc-blende crystal which has only (110) symmetry planes. A very interesting consequence of this is that in unreconstructed zinc-blende-type crystals the appearance of surface states in the energy gap next to the X point is not forbidden by symmetry. This is a consequence of the fact that the plane (110) is not a symmetry element of X and no symmetry argument can be applied to surface states in the energy gap next to the point X. Surface states for a zinc-blende crystal with a termination at a (110) plane for an energy gap next to the point X are therefore of the Tamm-Goodwin type.

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