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Energy dispersion of image states and surface states near the surface-Brillouin-zone boundary

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The nearly-free-electron model of surface-state occurrence in the the projected s,p-band gaps of metals is extended to the study of the energy dispersion near the boundaries of the surface Brillouin zone. The model is applied to available photoemission and inverse-photoemission data in the $\overline{\Gamma} \overline{Y} \overline{\Gamma}$ direction on Cu(110) and Ni(110). Good agreement is obtained for the energy dispersion away from \overline{Y} if z_0 , the image-plane distance, has been chosen to force agreement at \overline{Y} . In particular, the large effective masses (as high as 2.0*m*) which have been reported for the first image-induced surface state are explained.

I. INTRODUCTION

The systematics of surface-state occurrence within *s*,*p*band gaps of noble and transition metals have been described by a phase model based on a combination of elementary multiple-reflection theory and elementary nearly-free-electron theory.^{1,2} In this paper we extend this approach to the $E(k_{||})$ energy dispersion of surface states and image states. Applications of the phase model to the effective masses of surface states and image states near the *center* of the surface Brillouin zone (SBZ) have been presented elsewhere.^{1,3} We concentrate in this paper on bulk band gaps associated with reciprocal-lattice vectors **g** which are *not* perpendicular to the crystal surface. The projected gaps of concern are those which are centered on symmetry points at the SBZ boundaries.

As illustrative examples, we shall treat the surface states which occur along the $\overline{\Gamma} \overline{Y} \overline{\Gamma}$ direction in Cu(110) and Ni(110). These cases are especially interesting since *three* kinds of surface state have been observed along this direction using photoemission⁴ and inverse photoemission:⁵⁻⁷ the odd and even Shockley states and the first member of the image-state Rydberg series. The latter state has excited attention^{6,8} because it displays an unexpectedly large apparent effective mass. We shall show how the phase model can account for these data. We shall discuss the extent to which such analysis could lead to a determination of the shape of the surface-potential barrier.

II. REFLECTION PROPERTIES OF THE SURFACE BARRIER

A. Multiple-reflection model

In the multiple-reflection approach to surface-state formation, $^{9-11}$ an electron is visualized as being trapped between the crystal and the surface barrier. If $r_C e^{i\phi_C}$ and $r_B e^{i\phi_B}$ denote the reflectances at the crystal and surface barriers, respectively, we have $r_C = r_B = 1$, and the condition for existence of a surface state is

$$\phi_C + \phi_B = 2\pi n \quad , \tag{1}$$

15 APRIL 1987-I

where n is an integer. Strictly speaking, this is a onedimensional model applicable to the case where the Bragg reflection at the crystal is specular. We show below how this picture is modified when g, the Bragg-reflecting reciprocal-lattice vector, is off-normal.

An underlying assumption is that the surface barrier itself can be treated as one dimensional; i.e., it is a function only of the z coordinate perpendicular to the surface. Equivalently, the barrier-phase change ϕ_B can be treated as a function only of the perpendicular kinetic energy,

$$\varepsilon \equiv \hbar^2 \kappa^2 / 2m \equiv E - \hbar^2 k_{\parallel}^2 / 2m , \qquad (2)$$

where E is measured from the bottom of the innerpotential well, and κ is the perpendicular component of electron momentum.

B. ϕ_B and logarithmic derivatives

The phase change on electron reflection at the surface barrier must be evaluated with respect to some reference reflectance plane. The simplest case is that of a step barrier, for which we have

$$\tan(\phi_B/2) = -\left[(E_V - \varepsilon)/\varepsilon\right]^{1/2},\tag{3}$$

evaluated at the step itself. E_V is the vacuum level measured with respect to the bottom of the inner-potential well. More generally, we have

$$\kappa \tan(\phi_B/2) = l , \qquad (4)$$

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where l is the logarithmic derivative $(\dot{\psi}/\psi)$ of the wave function ψ on the vacuum side of the reference plane. For saturated image barriers, i.e., those which join continuously to the crystal potential, it is customary to integrate Schrödinger's equation along the z axis and to evaluate ϕ_B from the computed logarithmic derivatives.¹² The numerical integrations are readily carried out using a desk-top personal computer.

In this work we have used a model barrier devised recently by Jones, Jennings, and Jepsen¹³ (JJJ barrier). Explicitly, the surface barrier potential is given (in Rydberg units) by

$$V_{B}(z) = \begin{cases} -\frac{1}{2(z-z_{0})}(1-e^{-\lambda(z-z_{0})}), & z > z_{0}, \\ -\frac{U_{0}}{1+Ae^{\beta(z-z_{0})}}, & z < z_{0}. \end{cases}$$
(5)

 U_0 is the inner potential and z_0 is the position of the image plane relative to the z origin. The parameters $\beta = U_0/A$ and $A = -1 + 2U_0/\lambda$ are fixed by the requirements of smooth continuity. The free parameter λ is a characteristic distance over which the barrier changes from steplike to imagelike behavior.

III. FOUR-WAVE NEARLY-FREE-ELECTRON MODEL

To evaluate ϕ_C we adopt the simple nearly-free-electron (NFE) approach. We are concerned with projected bulk band gaps which are centered at the boundary of the surface Brillouin zone. We require four plane waves, ^{5,11,14} as opposed to the two plane waves adequate for gaps near the zone center associated with normal g vectors.

A. Projected bulk band gaps

For the sake of concreteness we consider in Fig. 1 the case near the \overline{Y} point at the SBZ of the (110) face of a face-centered-cubic metal. Two bulk reciprocal-lattice vectors are involved, $\mathbf{g} = (g_x, g_y, g_z)$ and $\mathbf{g}' = (g_x, g_y, -g_z)$. The four plane waves have vectors \mathbf{k} , $\mathbf{k} - \mathbf{g}$, \mathbf{k}' , and $\mathbf{k}' - \mathbf{g}'$, with $\mathbf{k} = (k_x, k_y, k_z)$ and $\mathbf{k}' = (k_x, k_y, -k_z)$. Bulk band energies in the NFE model are given by

$$\begin{vmatrix} \hbar^2 \mathbf{k}^2 / 2m - E & V_g \\ V_g & \hbar^2 (\mathbf{k} - \mathbf{g})^2 / 2m - E \end{vmatrix} = 0 , \qquad (6)$$

with a similar expression involving \mathbf{k}' and \mathbf{g}' . V_g is the appropriate Fourier component of the pseudopotential. The 4×4 secular equation reduces to two identical 2×2 equations because there are no Fourier components of the crystal potential which can diffract waves \mathbf{k} or $\mathbf{k} - \mathbf{g}$ into \mathbf{k}' or $\mathbf{k}' - \mathbf{g}'$.

Within the fundamental band gap, solutions with real E are possible but with complex $k_z = p - iq$. For an offnormal **g** vector, the solutions for p and q are given by



FIG. 1. Brillouin-zone diagram appropriate to the $\overline{\Gamma} \overline{Y} \overline{\Gamma}$ direction on Cu(110); g and g' are bulk reciprocal-lattice vectors and p is the real part of the perpendicular wave vector at k_{\parallel} .

the following expressions:

$$\eta^{3} + \frac{1}{4} [2(\gamma - 2\varepsilon) - g_{z}^{2}]\eta^{2} + \frac{1}{16} [\gamma^{2} - 2g_{z}^{2}(\gamma - 2\varepsilon) + 4V_{g}^{2}]\eta - g_{z}^{2}\gamma^{2}/64 = 0$$
(7)

and

$$(q^{2}+E)(2p-g_{z}) = p[(k_{x}-g_{x})^{2}+(k_{y}-g_{y})^{2} + (p-g_{z})^{2}] + (p-g_{z})(k_{x}^{2}+k_{y}^{2}+p^{2}).$$
(8)

where we have defined

$$\eta = (p - g_z/2)^2 , (9)$$

$$\gamma = g_x(g_x - 2k_x) + g_y(g_y - 2k_y) . \tag{10}$$

At the SBZ itself $(k_x = g_x/2, k_y = g_y/2)$ we have $p = g_z/2$, the bulk Brillouin-zone value. Away from the SBZ, p deviates from the bulk Brillouin-zone value, but only slightly (less than a few percent). The situation is illustrated in Fig. 1.

B. Wave-function matching

Inside the crystal the wave function will be some linear combination of the following two functions:

$$\psi_1 = e^{qz} [e^{ik_{||}r_{||}} \cos(pz+\delta) + \rho e^{ik'_{||}r_{||}} \cos(p'z-\delta)], \qquad (11)$$

$$\psi_2 = e^{qz} \left[e^{ik_{||}r_{||}} \sin(pz+\delta) + \rho e^{ik_{||}r_{||}} \sin(p'z-\delta) \right], \quad (12)$$

where $k'_{||} = k_{||} - g_{||}$, $p' = p - g_z$, and where ρ and δ are amplitude and phase factors associated with the eigenvec-

tors of Eq. (7). On the barrier side of the barrier-reference plane, we write the wave function as a linear combination of the form

$$\psi = \alpha_1 e^{ik_{||}r_{||}} \psi_{B_1}(z) + \alpha_2 e^{ik_{||}r_{||}} \psi_{B_2}(z) . \qquad (13)$$

Equating logarithmic derivatives at some matching plane z_M yields

$$\tan[(p-p')z_M + 2\delta] = \frac{p(-q+l') - p'(-q+l)}{pp' + (-q+l)(-q+l')}, \quad (14)$$

where *l* and *l'* are the logarithmic derivatives $\dot{\psi}_{B1}/\psi_{B1}$ and $\dot{\psi}_{B2}/\psi_{B2}$, respectively.

C. Multiple-reflection visualization

Waves k and k-g are now coupled into waves k' and k'-g' through reflection at the surface barrier. Defining the following phases, ϕ_C , ϕ_{B1}^* , and ϕ_{B2}^* ,

$$p \tan(\phi_{B1}^*/2) = l - q = \kappa \tan(\phi_{B1}/2) - q$$
, (15)

$$-p'\tan(\phi_{B2}^*/2) = l' - q = \kappa'\tan(\phi_{B2}/2) - q , \qquad (16)$$

$$\phi_C = g_z z_M + 2\delta , \qquad (17)$$

Eq. (14) reduces to

$$-\tan(\phi_C) = \tan(\phi_{B1}^*/2 + \phi_{B2}^*/2)$$
(18)

or, equivalently,

$$2\phi_C + \phi_{B1}^* + \phi_{B2}^* = 2\pi n , \qquad (19)$$

where *n* is an integer.

This expression can be visualized in terms of the multiple-reflection approach as depicted in Fig. 2. Reflections at the crystal are diffractive (i.e., they are Bragg reflections from planes associated with vectors \mathbf{g} and \mathbf{g}') with phase change ϕ_C . Reflections at the surface barrier are specular. In each complete cycle of multiple reflection, the electron approaches the surface barrier twice, but with different values, ε_1 and ε_2 , of the perpendicular energy:

$$\epsilon_1 = E - (\hbar^2/2m)(k_{||})^2$$
, (20)

$$\epsilon_2 = E - (\hbar^2/2m)(k_{||} - g_{||})^2$$
 (21)

We may rewrite Eq. (19) as

$$\phi_C + \langle \phi_B \rangle = \pi n , \qquad (22)$$



FIG. 2. Multiple-reflection visualization of the surface states. In each complete cycle of multiple reflection, the trapped electron approaches the surface barrier twice, experiencing the phase changes ϕ_{B1}^* and ϕ_{B2}^* ; reflections at the crystal are diffractive with phase change ϕ_C .

with $\langle \phi_B \rangle = (\phi_{B1}^* + \phi_{B2}^*)/2$. Note that Eq. (19) has been derived, rather than invoked from the multiple-reflection model. Note also the slight distinction between the phases ϕ_{B1}^* and ϕ_{B2}^* and the phases ϕ_{B1} and ϕ_{B2} obtained directly from the logarithmic derivatives.

D. Alternative bookkeeping method

To retrieve the results of Refs. 1 and 8 we may group the surface-state solutions in pairs. At the SBZ we have $\phi_{B_1}^* = \phi_{B_2}^* \equiv \phi_B$, and the quantization condition for surface-state existence becomes

$$\phi_{\overline{C}}^{\pm} + \phi_{B} = 2\pi n \quad , \tag{23}$$

with the proviso that there are now odd and even branches of the ϕ_C curve with $\phi_C^+ = \phi_C$ and $\phi_C^- = \phi_C + \pi$. Thus, we generate the same number of solutions even though the right-hand side of Eq. (23) is $2\pi n$, as opposed to πn in Eq. (22).

This maneuver is clearly a bookkeeping contrivance. It does, however, have some physical significance. The two n=0 solutions are the Shockley (or crystal-induced) surface states, which, for the case of a step barrier, are identical to the pair of surface states considered by Bartynski *et al.*⁵ The part of the wave function inside the crystal takes the form

$$\psi^{+} = e^{qz} \cos(\mathbf{g}_{||} \cdot \mathbf{r}_{||}/2) \cos(pz + \delta) , \qquad (24)$$

$$\psi^{-} = e^{qz} \sin(\mathbf{g}_{||} \cdot \mathbf{r}_{||}/2) \sin(pz + \delta) .$$
⁽²⁵⁾

For a repulsive pseudopotential $(V_g > 0)$ and for the δ values appropriate to this problem, the $s_{||}$ -like state ψ^+ , which puts its charge density on surface atoms, will lie higher in energy than the $p_{||}$ -like state ψ^- which puts its nodes on surface atoms. For $n \ge 1$ we have the image surface states, and these too will alternate between odd and even symmetry. For the remainder of this paper we shall use the bookkeeping system of Eq. (22) rather than the alternative odd/even pairwise system.

IV. APPLICATION TO Cu(110) AND Ni(110)

A. Surface barrier parameters

As indicated above, we have used the JJJ barrier. The internal parameters of this empirical barrier were chosen to force reasonable agreement for the surface-state energies at \overline{Y} . Figure 3 shows the graphical solutions appropriate to \overline{Y} on Cu(110). The energy of the lowest (n = -1) state at Cu(110) \overline{Y} is known to be $E_F - 0.39$ eV from high-precision angle-resolved photoemission work;⁴ the energy of the next lowest state is given variously as 2.0 eV (Ref. 15), 2.5 eV (Ref. 5), and 1.8 eV (Ref. 7) above E_F ; by extrapolation of the data of Ref. 7, we may place the energy of the third surface state (or first image state) at Cu(110) \overline{Y} in the energy window 5.5±0.4 eV above E_F .

This match at Cu(110) \overline{Y} was obtained with the following parameters: $z_M = 0$, where the origin is taken at the outermost atomic layer, and $z_0 - z_M = 2.4$ a.u. The parameters λ and U_0 were not treated as disposable, but were fixed at $\lambda = 0.9$ a.u., a value in the middle of the



FIG. 3. Graphical solutions for the lowest six surface states at \overline{Y} (solid curves and circles) and at the midpoint between $\overline{\Gamma}$ and \overline{Y} (dashed curves and open circles) showing the different kinds of dispersion.

range favored in Ref. 13; $U_0 = -11.4$ eV, the freeelectron value. In investigating the dispersion away from \overline{Y} , all parameters were frozen.

B. Bulk-band-structure parameters

The parameters governing the behavior of ϕ_C are the energies of the edges of the projected bulk band gap. These are taken from the known properties¹⁶⁻²⁰ of the bulk band structures. The parameter V_g is not a constant but has to be continually readjusted to fit the variation with $k_{||}$ of the width of the projected gap. There are complications associated with the proximity in energy of the *d* band, especially in Ni. On the other hand, we know from rather general theoretical considerations^{10,11} that ϕ_C



FIG. 4. Comparison between theory (solid curves) and experiment (open circles from Ref. 7, open squares from Ref. 5, dots from Ref. 4) for surface states in the $\overline{\Gamma} \overline{Y} \overline{\Gamma}$ direction on Cu(110). The projection of the bulk band structure is indicated by hatching.



FIG. 5. Comparison between theory (solid curves) and experiment (open circles from Ref. 6) for surface states in the $\overline{\Gamma} \ \overline{Y} \ \overline{\Gamma}$ direction on Ni(110). The projection of the bulk band structure is indicated by hatching.

must increase by π on traversing a projected bulk band gap. The approximate discussion of this paper rests on the assumption that the form of the variation of ϕ_C across the gap is not strongly model dependent.

C. Results

The calculated $E(k_{\parallel})$ dispersion relations for surface states in the $\overline{\Gamma} \overline{Y} \overline{\Gamma}$ direction on Cu(110) are compared with the available experimental data^{4,5,7} in Fig. 4. The overall agreement with experiment is seen to be reasonable. The corresponding comparison for Ni(110) $(z_0 - z_M)$ =2.4 a.u.) is shown in Fig. 5. Once again the overall agreement is reasonable. (The experimental data near the n = -1 state fall close to a predicted bulk direct transition,^{6,8} and so the identification of this experimental feature is ambiguous.⁸) The self-consistent slab calculations of Kleinman and co-workers on Cu(110) (Ref. 21) and Ni(110) (Ref. 22) are also in good agreement with the data for Shockley (n = -1,0) states; these calculations employ a short-range barrier and therefore do not generate the image states.

D. Conclusions and discussion

We conclude that if agreement for a surface-state energy has been obtained (or forced) at \overline{Y} , then agreement for the energy dispersion of that state across the SBZ is inevitable, at least within the currently attainable precision. In particular, the rather flat dispersion observed for the n = 1 image state^{6,7} is well reproduced by the model. It is therefore not necessary to invoke surface corrugation^{6,23} or many-body effects²⁴ to account for the large effective masses.

Adopting the colorful language of Pendry *et al.*,²⁵ we can describe the broad sweep of the results of Figs. 4 and 5 in terms of a "battle" between the crystal and the vacuum. The crystal is trying to pull the surface-state disper-

sion curve into a form characteristic of the crystal—in this case dispersing upwards away from \overline{Y} at a rate imposed by the projected bulk band gap. The vacuum, on the other hand, is pulling towards free-electron-like behavior—i.e., upwards dispersion centered on $\overline{\Gamma}$ with $m^*=m$. For the n = -1 state, it is clear that the crystal wins. For the higher states $(n \ge 2)$ of the Rydberg series it is clear that the vacuum wins; the dispersion curves for these states converge on the curves $E_V + \hbar^2 k_{\parallel}^2/2m$ or $E_V + \hbar^2 (k_{\parallel} - g_{\parallel})^2/2m$, whichever has the lower energy; and the effective mass is negative at \overline{Y} .

For n=0 and n=1, the contest is more evenly matched. The n = 0 state at \overline{Y} is a Shockley or crystalinduced state. It occurs for step barriers or other shortrange barriers and is the even s_{\parallel} -like counterpart of the odd p_{\parallel} -like n = -1 state. On approaching $\overline{\Gamma}$, however, the energy of this state approaches very closely that of the n=1 state, and it is perhaps more appropriate near $\overline{\Gamma}$ to regard it as part of the image-state Rydberg series. The n = 1 state is primarily imagelike, dispersing downwards away from \overline{Y} . Its dispersion curve, however, is severely distorted from free-electron-like form on traversing the projected bulk band gap. It is therefore an image state but with considerable crystal-induced character. There is thus a continuous gradation of behavior between the two extremes, and the theoretical possibility of a "drawn match" $(m^*/m = \pm \infty)$ cannot be excluded.

V. SURFACE-BARRIER DETERMINATION

For the (110) faces of Cu and Ni, we have achieved reasonable agreement for surface-state energies and dispersions using a JJJ barrier with an image-plane distance z_0 at 2.4 a.u. from the outermost atomic layer—that is to say, at 1.2 a.u. from the jellium edge. This value is comfortably close to the jellium range of values.^{26,27} We hesitate to draw a strong conclusion here for the following reasons.

Our numerical experiments with the JJJ barrier and other empirical barriers²⁸ have not yet produced an ansatz for the surface barrier which is *accurately* transferable over *all* five gaps on *all* three low index faces. Fitting the surface-state energies in a subset of these gaps *is* possible.^{1,2,28,29} The derived values of z_0 depend on the choice of ansatz—a lack of uniqueness well known from analyses of preemergent fine structures in low-energy electron diffraction.^{13,30,31} We are limited in this analysis by the crudity of the NFE representation of the crystal electronic structure. Also, requirement of self-consistency influences the energies of surface states, especially those which are partially occupied and which therefore enter into the determination of the self-consistent surface potential.

We conclude that gap-to-gap and face-to-face comparisons of surface-state energies are a promising way to refine the shape of the surface barrier, but that such work is best carried out in the context of self-consistent firstprinciples calculations. We repeat the observation made in Ref. 1 that the perpendicular energies of the dozen or so known surface states in NFE-type gaps on Cu span the entire range of the inner-potential well. Their accurate reproduction should impose strong constraints on any acceptable form for the surface barrier, especially in the interesting changeover region between steplike and imagelike behavior.

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APPENDIX: ANALYTICAL APPROXIMATIONS FOR IMAGE STATES

The main features of the image-state dispersion relations described above can be derived analytically with use of the WKB approximation for the barrier phase change. Ignoring the distinction between $\phi_{B1}^*(\phi_{B2}^*)$ and $\phi_{B1}(\phi_{B2})$, we write the WKB forms¹²

$$\phi_{B_1}^*/\pi = \frac{1}{2} [(1 \text{ Ry})/(E - \varepsilon_1)]^{1/2} - 1 ,$$

$$\phi_{B_2}^*/\pi = \frac{1}{2} [(1 \text{ Ry})/(E - \varepsilon_2)]^{1/2} - 1 .$$
(A1)

Solving for the energies in the vicinity of the SBZ boundary and expanding as far as $(k_{||} - g_{||}/2)^2$ yields

$$E = E_V - e_n + (\hbar^2/2m)(g_{||}/2)^2 + (\hbar^2/2m^*)(k_{||} - g_{||}/2)^2 ,$$

$$e_n = \frac{1}{4}(1 \text{ Ry})/(n+a)^2 ,$$

$$a = 1 - \phi_C/\pi ,$$

$$m/m^* = 1 - \frac{3}{4}(\hbar^2 g_{||}^2/2m)/e_n .$$

(A2)

Since $e_n \ll \hbar^2 g_{\parallel}^2 / 2m$, the effective mass is negative, as expected.

Near the center of the SBZ, it is clear that if ε_1 is close to E_V , ε_2 will be very small. We are then justified in setting $\phi_{B2}^* = -\pi$ to obtain

$$E = E_V - e_n + (\hbar^2 / 2m^*) k_{||}^2 ,$$

$$e_n = \frac{1}{16} (1 \text{ Ry}) / (n+a)^2 ,$$

$$a = 1 - \phi_C / \pi ,$$

$$m / m^* = 1 .$$
(A3)

The binding energy e_n therefore changes in going from $k_{||}=0$ to $k_{||}=g_{||}/2$, and there are two sources for this change: (i) the coefficient for e_n changes from $\frac{1}{16}$ to $\frac{1}{4}$ in Eqs. (A2) and (A3), and (ii) ϕ_C changes by π on traversing a projected band gap. Source (ii) is dominant and has been considered in a previous treatment of this problem.⁸

For the gaps considered here it is reasonable to take $g_z z_M = \pi/2$, whence we have $\phi_C = -\pi/2$ at the bottom and $\phi_C = +\pi/2$ at the top of the gap.^{1,8} The binding energy of the lowest image state n = 1 increases from 0.14 eV at $\overline{\Gamma}$ to 1.51 eV at the SBZ boundary. It is this increase in e_n which flattens the dispersion curve and accounts for the large effective masses which have been obtained experimentally: $m^*/m = 1.7 \pm 0.3$ Ni(110) (Ref. 6) and 2.0 ± 0.4 on Cu(110) (Ref. 7). The $E_n(k_{||})$ curves are not parabolic, and so it is not strictly permissible to characterize the dispersion by a single effective mass. What the experimentalists really mean here is that the overall energy dispersion is less than free-electron-like by a factor designated as m/m^* .

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