

contrast to the Ising limit ( $p = 1$ )  $G_R$  acquires a positive gap to  $O(|r|^2)$  for  $p > 1$ .

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## Origin of Surface Resonance States in Nearly-Free-Electron Metals: Al(001)

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Thin-film energy-band determinations of a surface-state-surface-resonance band in Al(001) are found to account completely for and clarify the new angle-resolved photoemission observations of Gartland and Slagsvold. The transition from a true surface state to a surface resonance is explained in terms of a mechanism in nearly-free-electron metals for the formation of surface resonances in "partial" Bragg-reflection bulk energy gaps.

The first directly observed occupied surface state on any simple nearly-free-electron (NFE) metal was very recently reported by Gartland and Slagsvold<sup>1</sup> using angle-resolved photoemission measurements on the (001) face of aluminum. A dominant surface-sensitive peak was interpreted as emission from a two-dimensional band of surface states. Spectra recorded along the  $\bar{\Gamma}-\bar{X}$  line in the two-dimensional Brillouin zone yielded an experimental dispersion relation for this peak which is parabolic with an effective mass  $m^* = (1.03 \pm 0.1)m$ . By comparison with the projected bulk band structure<sup>2</sup> along  $\bar{\Gamma}-\bar{X}$ , the experimental band starts in the bulk gap at  $\bar{\Gamma}$  and rises up in this gap. At about  $\vec{k}_{\parallel} = (0.5, 0)$  (units  $\pi/a$ , where  $a$  is the surface lattice parameter) it merges into the continuum region and continues smoothly upward to cut  $E_F$  at about  $\vec{k}_{\parallel} = (0.8, 0)$ . While true surface states can exist only in an absolute bulk band gap, the experimental peak shows no effect due to the closing of the absolute gap at about  $\vec{k}_{\parallel} \sim (0.5, 0)$ , but persists smoothly into the continuum region and up to  $E_F$ . A calculation by Pendry<sup>3</sup> of the angle- and energy-resolved photocurrent also showed no changes in the intensity or peak width when the peak leaves

the bulk band gap, in good agreement with experiment. Gartland and Slagsvold, therefore, suggested that the existence of the peak for large values of  $k_{\parallel}$  indicates a transition from a true surface state to a surface resonance. These authors were not able, however, to correlate the observed peak behavior for large  $k_{\parallel}$  with the results of existing surface electronic band calculations<sup>2,4</sup>; however, the measured dispersion relation agrees quite well with the behavior of the surface state found in these calculations for  $\vec{k}_{\parallel} < (0.5, 0)$ .

In this Letter we present thin-film results for the electronic structure of the aluminum (001) surface which completely account for and clarify the experimentally observed behavior. Using our recently developed film linearized augmented plane-wave (LAPW) method,<sup>5</sup> we have performed non-self-consistent calculations for nine- and thirteen-layer aluminum films. We find a surface-state-surface-resonance band which is in very good agreement with the measured dispersion relation and we theoretically explain the observed transition from a true surface state to a surface resonance in terms of a mechanism (which is particularly transparent) in NFE metals for the formation of a surface resonance in

“partial” Bragg-reflection bulk energy gaps. We also suggest that a similar mechanism may account for the occurrence of a similar class of surface resonances in more complex systems such as semiconductors and transition metals.

Figure 1(a) shows projected bulk free-electron bands,  $E(\vec{k}_{\parallel}) = (\vec{k}_{\parallel} + k_z \hat{z} + \vec{G})^2$ , for a few fixed values of  $k_z$ , the  $z$  component of the three-dimensional Bloch momentum. Here,  $\vec{k}_{\parallel}$  and  $k_z$  refer to the slab-adapted<sup>2</sup> (three-dimensional) Brillouin zone (BZ), and the three-dimensional reciprocal lattice vector,  $\vec{G}$ , refers to the primitive BZ. In Fig. 1(b) we have reproduced from Ref. 2 those projected bulk bands with the same values of  $k_z$  displayed in Fig. 1(a). Absolute bulk band gaps are represented by the shaded regions. The band structure for the nine-layer Al(001) film, shown in Fig. 1(c), was calculated 41  $k_{\parallel}$  points along  $\bar{\Gamma}-\bar{X}$  to about 10 mRy accuracy using the film-muffin-tin (FMT)<sup>5</sup> potential. The plus and minus signs in Fig. 1(c) label states which are, respectively, symmetric and antisymmetric

with respect to  $z$  reflection (i.e., in the central plane of the film). We want to emphasize that the film bands, although seemingly complicated at first glance, are essentially free-electron-like as can be seen from the following. Turning on the bulk crystal potential causes bands with the same value of  $k_z$  in Fig. 1(a) to repel one another (all the bands shown in Fig. 1 have the same two-dimensional  $\bar{\Delta}_1$  symmetry, i.e., there are no  $\bar{\Delta}_2$  bands in the energy range shown) and this causes bulk energy gaps to appear. The resulting band structure, pictured in Fig. 1(b), remains predominantly parabolic as expected for a NFE metal like aluminum. Introducing the perturbation due to the presence of the surface destroys periodicity in the  $z$  direction with the result that  $k_z$  is no longer a good quantum number. Crossings of bulk bands with different  $k_z$  in Fig. 1(b) must now become anticrossings in the film calculation, Fig. 1(c). The only allowed crossings in Fig. 1(c) are between states of different  $z$ -reflection symmetry. As the film becomes thicker, however,

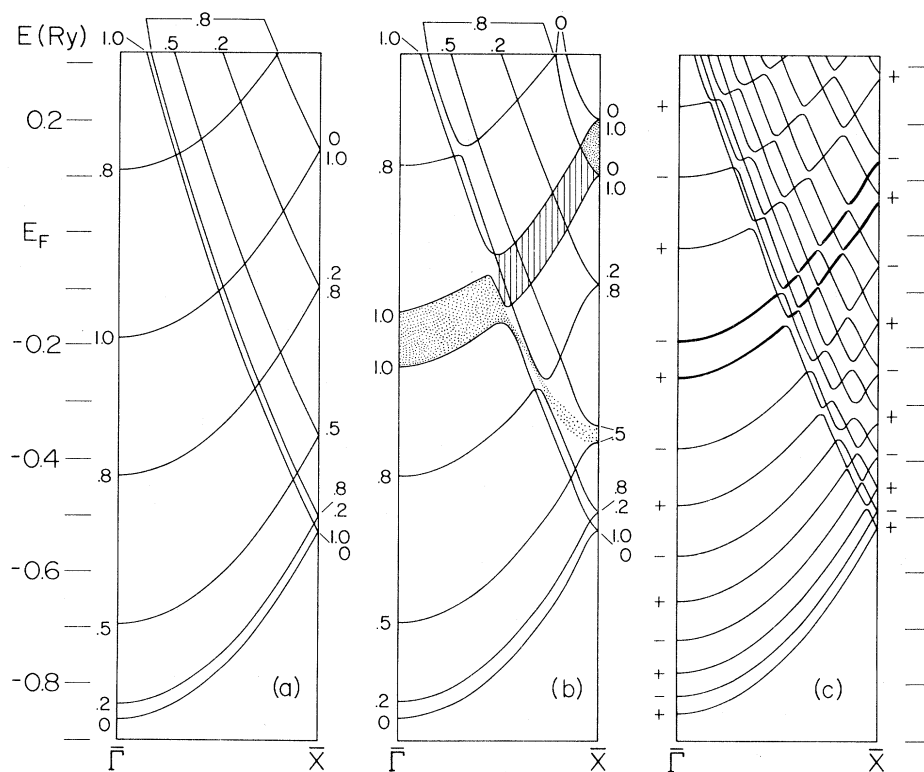


FIG. 1. (a) Free-electron bulk hands. (b) Projected bulk bands (Ref. 2). Absolute bulk band gaps are represented by the shaded regions. A “partial” Bragg-reflection gap is represented by vertical cross hatching. (c) Band structure for a nine-layer Al(001) film. The relevant pair of the surface states and surface resonances are identified by the heavy lines. The numbers which label the bands in (a) and (b) represent values of  $k_z$  in units of  $2\pi/A$ , where  $A$  is the bulk lattice parameter.

$k_z$  is more nearly a "good" quantum number, and these additional sharp anticrossings begin to look more and more like true crossings. In view of these remarks, one can see the close similarity of our film bands [Fig. 1(c)] with the projected bulk bands [Figs. 1(a) and 1(b)]. The other new feature in the film calculation is the occurrence of surface states and surface resonances.

For comparison with the experiment, the relevant pair of surface states and surface resonances are identified in Fig. 1(c) by heavy lines which clearly have a free-electron-like dispersion. The surface states start at  $\bar{\Gamma}$  and run up to about  $\bar{k}_{\parallel} = (0.5, 0)$  within a region corresponding to the absolute bulk band gap in Fig. 1(b). These surface states then persist as a pair of surface resonances into a region corresponding to the continuum of bulk states and within the partial Bragg reflection gap in Fig. 1(b) (represented by the vertical crosshatching), again becoming true surface states as they enter the smaller absolute band gap near  $\bar{X}$ . In agreement with the results of Caruthers, Kleinman, and Alldredge,<sup>2</sup> we find two pairs of surface states in this gap; one of these pairs is the continuation of the resonance states. While these surface states have been previously found,<sup>2,4</sup> this report focuses for the first time on the existence of the surface resonance. The dispersion of the heavy lines in Fig. 1(c) agrees extremely well with the experimental dispersion relation. The comparison is summarized in Table I. The average values of the symmetric and antisymmetric states listed in Table I are indicators of the limiting values as the film gets thicker (and the energy splitting between the surface states and surface resonances approaches zero); the agreement with experiment is remarkably good here. The experiment, which is sensitive to states localized near the surface, thus detects a true surface state for  $\bar{k}_{\parallel}$  less than about  $(0.5, 0)$  and a surface resonance for larger  $\bar{k}_{\parallel}$ , confirming the interpretation of Gartland and Slagsvold.

Figure 2 plots representative charge densities

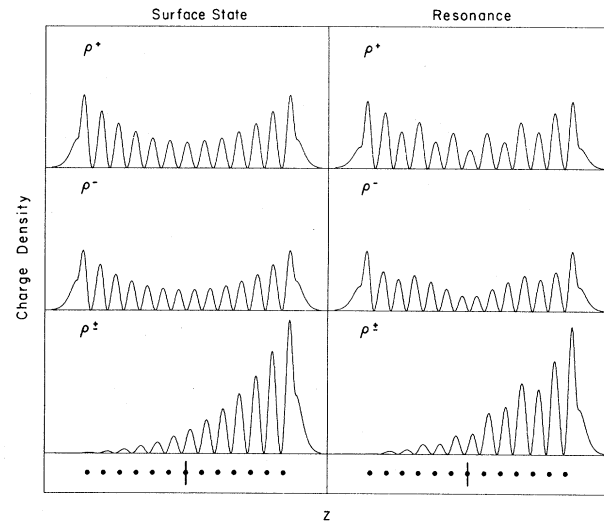


FIG. 2. Representative charge densities for the surface state [ $\bar{k}_{\parallel} = (0, 0)$ ] and surface resonance [ $\bar{k}_{\parallel} = (0.72, 0)$ ] calculated for a thirteen-layer Al(001) film. All charge densities are plotted for fixed  $\bar{r}_{\parallel} = (a/2, 0)$  where  $a$  is the two-dimensional lattice parameter. The heavy dots at the bottom indicate the layer spacing in the film. The first two panels in each column show  $\rho^+$  and  $\rho^-$  for the symmetric and antisymmetric states, respectively. The third panel shows the charge density of a linear combination of the even- and odd-parity states,  $\rho^{\pm} = \frac{1}{2} |\psi_{\pm} \pm \psi_{\mp}|^2$ , forming states localized on only one of the surfaces.

for the surface states and surface resonances, calculated for a thirteen-layer film. In the present version of our film LAPW method, all the basis functions are forced to have vanishing  $z$  derivative at boundary surfaces which are tangent to the two surface layers of muffin-tin spheres.<sup>5</sup> While this is not an essential feature of the method, it causes the wave functions in this calculation to have the zero derivatives at these surfaces seen in Fig. 2. The decay constant for the symmetric (+) surface state at  $\bar{\Gamma}$  is in very good agreement with that given in Ref. 2 for a 39-layer film. The surface state and surface resonance both exhibit essentially the same degree of localization near the surface. This ac-

TABLE I. Comparison of the experimental and theoretical (nine-layer film) surface state-surface resonance (SS-SR) for Al(001) along  $\bar{\Gamma}$ - $\bar{X}$  (energies in eV).

	(-) SS-SR	(+) SS-SR	Average	Expt. (Ref. 1)
$E_F - E_{SS}(\bar{\Gamma})$	2.53	3.41	2.97	$2.80 \pm 0.2$
$m^*/m$	$1.04 \pm 0.03$	$1.04 \pm 0.03$	1.04	$1.03 \pm 0.1$

counts for the absence of any abrupt change in the experimentally observed<sup>1</sup> and theoretically calculated<sup>3</sup> peak behavior due to the closing of the absolute bulk band gap near  $\vec{k}_{\parallel} = (0.5, 0)$ .

We offer a simple explanation for the occurrence of the surface state-surface resonance. Referring to Fig. 1(b), the absolute bulk band gap which starts at  $\bar{\Gamma}$  and continues to about  $\vec{k}_{\parallel} = (0.5, 0)$  is, in a simple pseudopotential model, a Bragg-reflection gap due to the  $V_{002}$  pseudopotential coefficient which splits the two degenerate plane-wave states with  $k_z = 1$  in Fig. 1(a). While the absolute gap is narrowed and pulled down in energy near  $\vec{k}_{\parallel} = (0.5, 0)$  (it continues downward to  $\bar{X}$  as a  $V_{111}$  absolute gap), the  $V_{002}$  Bragg gap persists as a partial  $V_{002}$  Bragg gap all the way up to the other absolute  $V_{002}$  gap at  $\bar{X}$ . This partial Bragg gap is delimited by the two NFE-like states with  $k_z = 1$  in Fig. 1(b). It is a partial gap in the sense that, while it is embedded in a continuum of bulk plane-wave states of the type  $(\vec{k} - \vec{G}_{111})$ , there are no bulk plane-wave states of the type  $(\vec{k})$  or  $(\vec{k} - \vec{G}_{002})$  in this partial Bragg gap. Introducing the perturbation due to the presence of the surface has the effect, then, of pulling into this  $V_{002}$  gap states from the continuum of  $(\vec{k})$  and  $(\vec{k} - \vec{G}_{002})$  states. In the region where it is an absolute Bragg gap, these states are true surface states, but in the region where it is a partial Bragg gap, these states are surface resonances, since they can mix with the continuum of  $(\vec{k} - \vec{G}_{111})$  states. Inside the partial Bragg gap, the  $(\vec{k})$  and  $(\vec{k} - \vec{G}_{002})$  character of these states must be localized near the surface, since only  $(\vec{k} - \vec{G}_{111})$  character is permitted deep into the bulk, and this favors the formation of a surface resonance. This interpretation also accounts for the fact that, like the surface state, the surface resonance in Fig. 2 exhibits oscillations normal to the surface which are characteristic of plane waves with  $k_z = \pm 1$ .

The formation of surface resonances in partial Bragg reflection gaps in NFE metals is a particularly striking and illustrative example of a general mechanism which can also be present in more complex systems. Thus, one could gener-

ally expect to find surface resonances at points in the two-dimensional BZ where (in the corresponding projected bulk band structure for a single two-dimensional symmetry type, e.g.,  $\bar{\Delta}_1$ , or  $\bar{\Delta}_2$  along  $\bar{\Gamma} - \bar{X}$ ) a bulk band edge of one "character" is embedded in a continuum of bulk states of another character.<sup>6</sup> While in NFE-like metals it is particularly easy to map such partial gaps (since the character of the bulk states is simply related to their plane-wave composition), a similar mapping for general systems would require inspection of projections of individual bulk bands. This could prove useful not only as a relatively simple model for predicting the occurrence of this class of surface resonances in complicated calculations of surface electronic structure, but also as a guide for experiments searching for states which are localized near the surface.<sup>7</sup>

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<sup>6</sup>In their general review, J. A. Appelbaum and D. R. Hamann [*Rev. Mod. Phys.* **48**, 479 (1976)] refer to this type of situation.

<sup>7</sup>In a preprint (for which we are grateful) received after completion of this paper, G. V. Hansson and S. A. Flodström (*Phys. Rev. B*, to be published) confirm the results of Ref. 1 and report emission from an Al(111) surface resonance band. Using an approximate projection of the bulk bands, they have noted that the experimentally determined surface resonance states occur in what they call "filled band gaps."