Effects of Different Potentials on Iron Surface States*

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We report first-principles calculations at $\bar{\Gamma}$ for a (001) iron thin film. Four different potentials have been investigated, and we find for the first time that the existence and symmetry of surface states depends crucially on details of the potential. For the potential which we consider most physical we find a surface state which peaks more than one-half layer outside the last plane of atoms.

In this paper we present the results of a surface-state calculation at the center ($\bar{\Gamma}$) of the two-dimensional (2D) Brillouin zone of a (001) Fe film. We have discovered the first reported surface state which peaks more than one-half layer outside the last plane of atoms. We have also discovered that the $\bar{\Gamma}$ surface states are very dependent on small changes in the potential. This is the first material investigated which shows this dependence.

We found these results by extending to transition metals the method of calculating thin-film eigenvalues and eigenfunctions which we developed for Li[1,2] and Al,[3-6] and which has been applied by Chelikowsky and co-workers to Al[7,8] and Si.[8] We use a basis set consisting of symmetrized combinations of plane waves, as in Refs. 1–6. Then, as in the rapidly converging supplemented orthogonal-plane-wave (OPW) method which we recently developed,[9] these plane waves are orthogonalized to the core wave functions, and supplemented with d-like functions existing within a "muffin tin" (MT) radius of each atomic site. This method allows us to investigate the effects of a variety of potentials, as we did in Al,[6] and can be extended to the self-consistent calculations which we shall presently show to be necessary for a detailed understanding of transition-metal surfaces.

We have performed first-principles calculations at $\bar{\Gamma}$ for four different potentials: (I) A warped MT (WMT) potential was calculated by overlapping $3d^7 4s^1$ atomic Coulomb potentials and calculating exchange by overlapping atomic charge densities and using a Taylor series expansion of $\rho^{1/3}$. We included second-order terms in this expansion and found that they affected the total potential by less than 0.1%.[10] The full Slater exchange approximation ($X\alpha$, with $\alpha = 1$) was used throughout this calculation. (II) A WMT calculation was performed, as in (I), except that the Coulomb potential V_C due to the $4s$ electrons was adjusted (as in Ref. 3) to give the right work function,[11] and to fall off like the $r_s = 2.66$ jellium[12] $V_C(z)$ beyond the jellium edge. (III) A WMT potential was constructed as in (II), except that the Kohn-Sham exchange approximation ($\alpha = \frac{2}{3}$) was used throughout the calculation. (IV) We adjusted model (II) to give a "Cambridge" potential—an unwarped MT potential which goes discontinuously to zero outside the last MT sphere. In all models calculations were performed on a thirteen-layer film, with the wave functions forced to go to zero three and one-half layers outside the last plane of atoms. We expanded in the (0,0), (1,0), (1,1), (2,0), and (2,1) two-dimensional symmetrized combinations of OPW's with 33 values of k_z plus the five d-basis functions. For model (II) we repeated the calculation with one fewer 2D symmetrized combinations of OPW's and ten fewer k_z and [excluding $\bar{\Gamma}_4$ which contains only one 2D symmetrized combination of OPW's below the (2, 1)] we found the most poorly convergent level only 0.017 Ry higher. We also increased

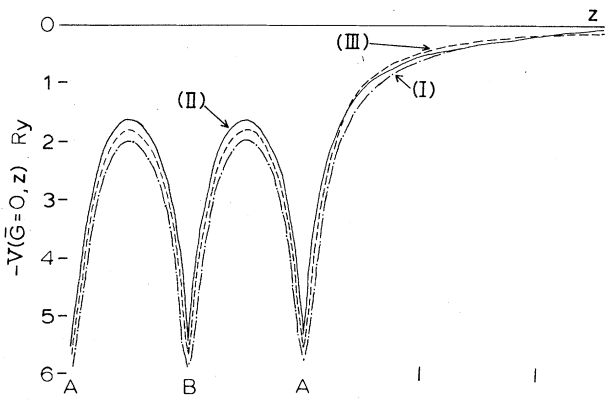

FIG. 1. The planar average [$\bar{G} = (0,0)$ Fourier transform] of model potentials (I), (II), and (III), plotted as a function of the direction normal to the thin-film surface. The potentials achieve their bulk values two layers inside the surface.

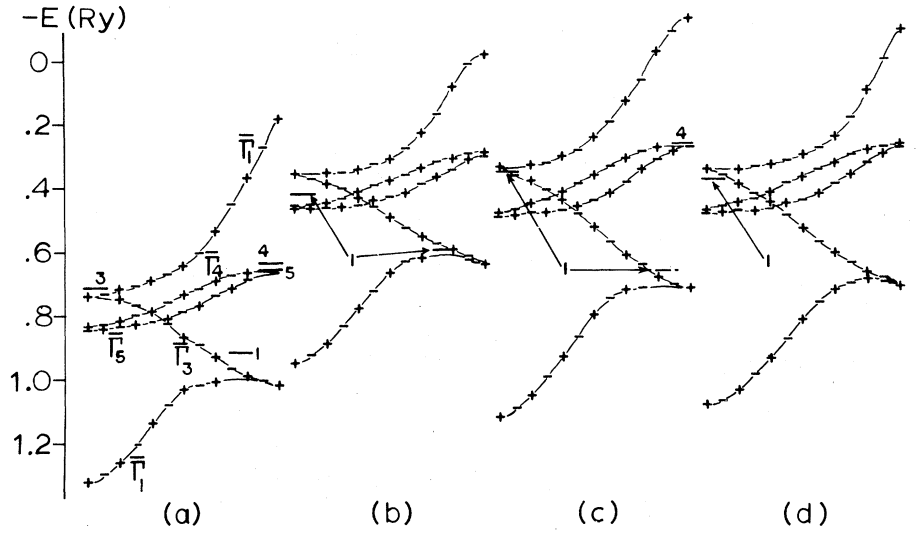

FIG. 2. $\bar{\Gamma}$ eigenvalues of various symmetries, plotted at equal intervals to show their similarity to bulk eigenvalues. Plusses and minuses denote states of even and odd parity with respect to reflection through the center of the plane. Pairs of surface states are indicated by long horizontal lines and are labeled by symmetry. (a) Model (I). (b) Model (II). (c) Model (III). (d) Model (IV). $E_F \approx -0.7$ Ry for (a) and $E_F \approx -0.33$ Ry for (b), (c), and (d).

the selvage region by one layer (using 36 k_z's) for $\bar{\Gamma}_1$ and found a maximum change of 0.0008 Ry for states more than 0.2 Ry below the vacuum. In Fig. 1 we show the planar average of potentials (I), (II), and (III) over the last few occupied layers and the beginning of the vacuum region. Note that potential (III) with $\alpha = \frac{2}{3}$ falls off most rapidly right outside the film. But because $\alpha = \frac{2}{3}$ gives a weaker atomic potential, its atomic charge and exchange tail extend further out than the others.

In Fig. 2 we show the $\bar{\Gamma}$ eigenvalues for each potential, plotted at equal intervals to show the relation to the bulk energy bands. Surface states are indicated by long horizontal lines and are labeled according to symmetry. We believe model (II) to be the most physical, and the results shown in Fig. 2(b) to be most representative of a real film. In model (I) the long atomic Coulomb tail was uncorrected and gave much too large a work function. Model (II) not only has about the right work function but also agrees well with the Δ_1 band gap in Wood's $\alpha = 1$, 3D augmented-plane-wave calculation.[13] Model (III) gives a much wider $\bar{\Gamma}_1$ band gap than that found in Tawil and Calloway's 3D calculation with $\alpha = 0.64$.[14] Model (IV) is clearly unphysical, but the ease of performing analytic calculations on such models leads to their frequent adoption.[15-19] For (001) Al we found[6] that changing from a realistic potential to a Cambridge potential had no significant effect on the surface states, but that is not the case here. The lower $\bar{\Gamma}_1$ surface state disappears into the lower $\bar{\Gamma}_1$ band as a result of the discontinuous potential.

The only two surface states for model (II) are of $\bar{\Gamma}_1$ symmetry, and are s-d hybrids. This is in general agreement with Kasowski's work on W and Mo,[20] materials with d-band widths similar to that of iron. But our wave functions, plotted in Figs. 3(a) and 3(b) as a function of planar position ($\bar{r}$) and normal direction (z), are somewhat different from his. Notice especially in Fig. 3(b) that the upper $\bar{\Gamma}_1$ surface state peaks outside the jellium edge, almost where the next occupied layer would be. Note also that this surface state is more localized in both the $\bar{r}$ and z directions than the lower-energy surface state. As we have noted before,[21] the $\bar{\Gamma}_1$ band gap disappears as one goes away from $\bar{\Gamma}$ in the 2D Brillouin zone and there can be no true surface state without a band gap. However, a tight-binding calculation[22] indicates that these surface states become resonances which persist over large areas of the 2D Brillouin zone around $\bar{\Gamma}$. Because of their transverse momentum, surface states at other points in the 2D Brillouin zone are not expected to extend so far beyond the crystal surface. Therefore the upper $\bar{\Gamma}$ surface state may play a major role in the catalytic activity of iron and other transition metals.

Looking at Fig. 2 we can conclude that any rea-

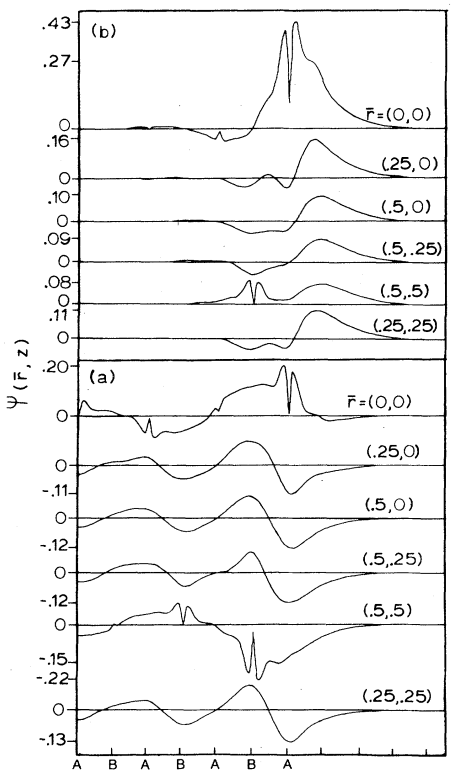

FIG. 3. The wave functions for (a) the lower and (b) the upper $\bar{\Gamma}_1^+$ model-(II) surface states are plotted for six different planar ($\bar{r}$) positions. The heights of the surface peaks and shoulders are indicated at the left. Orthogonalization contributions which would obscure the sharp 3D structure are intentionally omitted.

sonable model of the potential shows that the surface perturbation produces surface-localized wave functions. But small changes in the model cause surface states of various symmetries to appear and disappear. While model (II) probably provides a realistic first approximation to the potential, any investigation of transition-metal surfaces which hopes to understand the details of surface reactions must include self-consistent calculations.

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