Prediction of Electronic Surface States in Layered Materials: Graphite

M. Posternak and A. Baldereschi[a]
Institut de Physique Appliquée, Ecole Polytechnique Fédérale, CH-1015 Lausanne, Switzerland

and

A. J. Freeman and E. Wimmer[b]
Department of Physics, Northwestern University, Evanston, Illinois 60201
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Thin graphite films consisting of up to 25 atomic layers are studied with self-consistent local-density all-electron theory and model-potential calculations. Unoccupied surface states confined in the direction of the c axis are predicted at 3.8 eV above the Fermi energy. They are split off from the bulk free-electron interlayer band. These results provide a convincing interpretation of the surface states found in recent inverse photoemission experiments by Fauster *et al.*

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Recent inverse photoemission measurements on graphite by Fauster *et al.*[1] have provided detailed information on low-energy unoccupied states. Two kinds of features have been observed: (i) structure arising from states with a strong dispersion in the direction perpendicular to the basal plane (c axis), described by several authors[2-5] and recently interpreted by us as three-dimensional interlayer states,[5] and (ii) structure at lower energy (3.6 eV above the Fermi energy E_F), with negligible c dispersion. The question was raised[1] whether feature (ii) is due to indirect transitions into the bottom of a bulk band or to the presence of a surface state.

In this Letter, we present a consistent theoretical picture of surface states in graphite. We find unoccupied surface states 3.8 eV above the Fermi level, and provide a convincing interpretation of the inverse photoemission results of Fauster *et al.*[1] To our knowledge this is the first report of surface states in layered materials, where bands with strong c dispersion, from which surface states could derive, are not a common feature.

We have studied the formation of a surface state for a sequence of isolated graphite thin films with an odd number N of layers ranging from 1 to 25. Considering that the interlayer coupling in graphite is weak, we assume bulk graphite lattice parameters ($a = 4.648\,75$ a.u. and $c = 6.330\,61$ a.u.) and A-A stacking for all systems. The existence of surface states should not be affected by these assumptions. Electronic energies and wave functions of the systems with $N \leq 5$ have been computed with the all-electron local-density self-consistent full-potential linearized augmented plane-wave (FLAPW) method for thin films.[6] Thicker slabs and the reference infinite crystal have been studied with a model potential derived from the FLAPW results.

As expected, the characteristic occupied σ- and π-bonding states are obtained for the one-, three-, and five-layer systems and will be of no further concern in this Letter. The eigenvalues at Γ of all unoccupied states below the vacuum zero are displayed in the (lower) right-hand side of Fig. 1. Going from one to five layers, the two lowest eigenvalues, which have opposite z-reflection symmetry, converge to the energy of a surface state. Their nature as surface states becomes evident from their single-state charge densities given in Fig. 2 for the monolayer, and in Figs. 3(a) and 3(b) for $N = 5$. The two states shown in Figs. 3(a) and 3(b) have a high charge density outside the surface layer. However, for this film thickness they still interact, as is indicated by the difference in their energies (-70 mRy versus -62 mRy) and wave functions. Figure 3(c) shows the charge density of the next state (-5 mRy) which is even under z reflection. This state has interlayer bulk character and should correspond to the bulk band edge. Thicker slabs are necessary to obtain (i) negligible interaction between surface states and (ii) information on bulk states in the same energy range. Fortunately, the states of interest have strong free-electron-like character parallel to the atomic planes (cf. Figs. 2 and 3), and thus lend themselves to a simplified treatment by a model potential; a FLAPW treatment of slabs consisting of more than five layers would be prohibitively time consuming.

Our one-dimensional model is defined from the three-dimensional FLAPW potential and wave functions calculated for the monolayer. These are

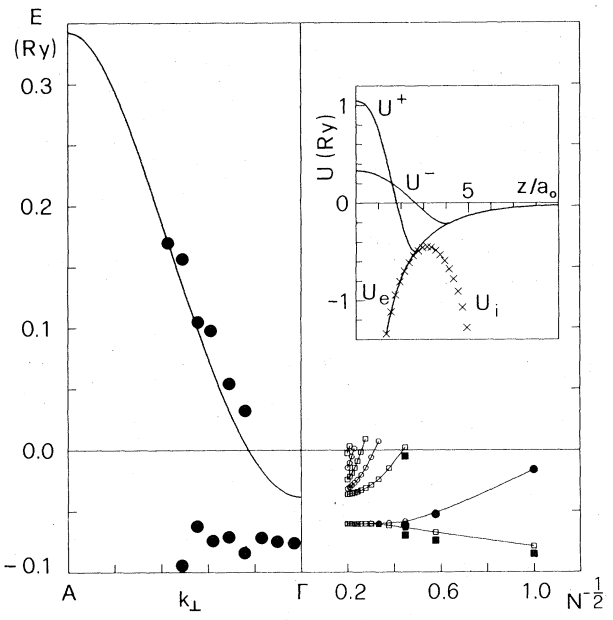

FIG. 1. Right panel: band energies at Γ of the empty states below vacuum zero for N-layer graphite slabs. Even (odd) states are indicated with squares (circles). Solid (open) symbols indicate FLAPW (model) results. Left panel: Γ-A dispersion of the interlayer band for the infinite model graphite crystal. Solid circles represent data of Fauster *et al.* (Ref. 1). Inset: model potentials U_e, U_i, U^+, and U^- derived from planar averaging of FLAPW results.

projected through x-y planar averaging onto the one-dimensional electrostatic potential $U_e(z)$ and wave functions $\Phi^{\pm}(z)$ (the $\pm$ refers to parity under z reflection). Then nonlocal norm-conserving monolayer potentials $U^{\pm}$ are obtained by constructing pseudo wave functions from the functions $\Phi^{\pm}$ near the atomic planes and inverting the Schrödinger equation.[7] We write the effective potentials $U^{\pm}$ as the sum of the local potential U_e and an orthogonality repulsion part: $U^{\pm} = U_e + U^{\pm}_{\text{orth}}$. The potentials U^+, U^-, and U_e are displayed in the inset of the right panel of Fig. 1. Potentials of multilayer films cannot be constructed as superpositions of these monolayer model potentials, because of mutual layer-layer polarization which modifies U_e in between the layers. Planar-averaged FLAPW potentials for three- and five-layer slabs show, however, that the interior electrostatic potential U_i (cf. Fig. 1), though different from U_e, does not depend on the number of layers N, and that the exterior potential is the same as for the monolayer. Therefore, the effective potentials for multilayer slabs are taken as the sum of an electrostatic part equal to U_i inside the film and U_e outside, and of a nonlocal orthogonality potential equal to the superposition of $U^{\pm}_{\text{orth}}$ centered on each layer site.

This nonlocal model potential has been used to study films with an odd number of layers ($N \leq 25$) and the infinite periodic system. We use plane waves as basis functions for the periodic system and uniformly distributed Gaussians of given width for the films. The model reproduces within 7 mRy the FLAPW energies (cf. Fig. 1). Comparison of their charge densities for $N = 1$ and 5 is displayed in Figs. 2 and 3. The resulting energies for $1 \leq N \leq 25$ and for the infinite system are collected in Fig. 1. The slab results (right-hand side of Fig. 1) clearly show (i) the formation of a pair of surface states for thick systems, and (ii) the condensation of levels at higher energies corresponding to the formation of the bulk interlayer band projected onto the two-dimensional Brillouin zone. This result is confirmed by the infinite-system calculation (solid line,

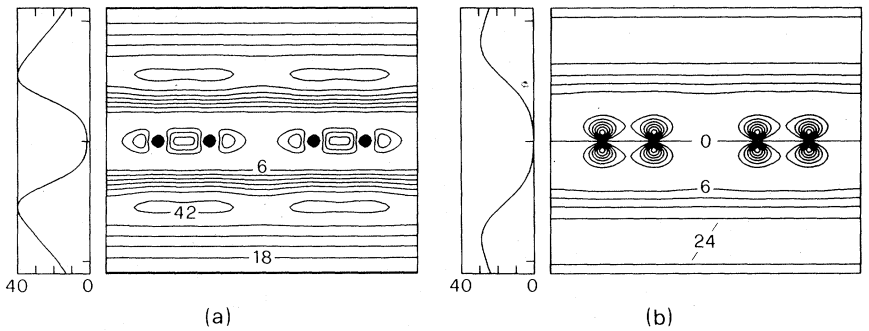

FIG. 2. Contour maps of the FLAPW charge densities of the (a) even and (b) odd empty states below vacuum zero for a graphite monolayer. Charge densities are in units of $10^{-3}\ e/\text{Å}^3$ and are represented in a plane perpendicular to the layer. The linear plots give the corresponding model densities. The tick marks on the vertical axis indicate multiples of the c parameter.

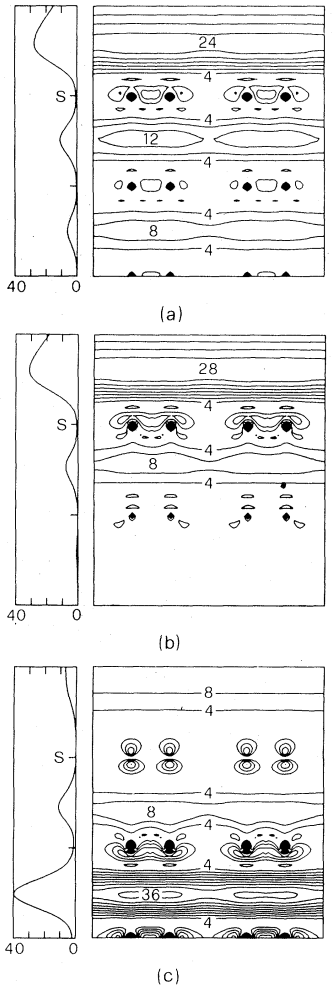

FIG. 3. FLAPW charge densities of the empty states below vacuum zero for a five-layer graphite slab. (Same notation and units as in Fig. 2.) (a) Lower even state, (b) odd state, and (c) upper even state.

left-hand side of Fig. 1), which shows the existence of a bulk band with large c dispersion. The bottom of this band corresponds to the discretely spaced levels obtained for the finite films. For $N \geq 13$ the interaction between the surface states on the two surfaces of the slab is negligible and the eigenvalues of the even and odd partners become quasidegenerate (their splitting is 0.1 mRy for $N = 13$). The eigenvalues are located in an absolute energy gap, so that they are true surface states at Γ. Figure 4 shows the charge density of the surface state for $N = 13$; it extends about three layers into the bulk.

The experimental data of Fauster *et al.* are reproduced in the left-hand side of Fig. 1, using E_F as reference energy. Comparison with our results shows the following: (i) The experimental structure which is independent of photon energy (i.e., nondispersed final states) corresponds to transitions into the surface state. (ii) In agreement with the findings of Ref. 1, the experimental structure which is strongly dependent on photon energy corresponds to transitions into the highly dispersed interlayer band lying above the surface state.

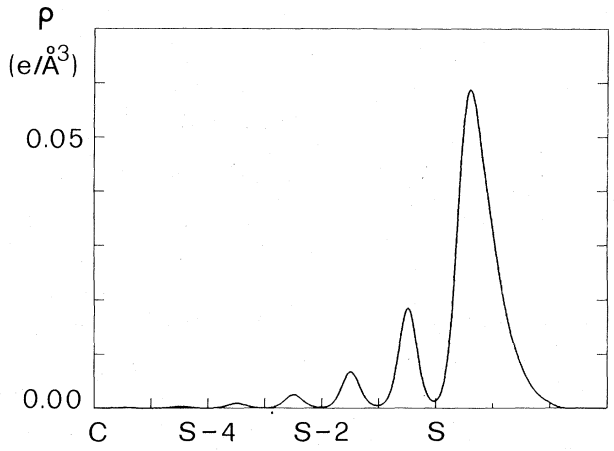

FIG. 4. Charge density of the right-hand-side surface state for a thirteen-layer graphite slab. The surface layer is indicated by S and the central layer by C.

To understand the existence of the surface state, one has to consider (i) the large extension in the c direction of the states bound to a single layer (Fig. 2 shows that their charge density is still large at distances from the layer of the order of the c parameter), and (ii) the strong orthogonalization potentials felt by an electron at each atomic layer. Orthogonalization effects on such extended wave functions are stronger in the interior than in the vacuum because of the additional orthogonalization to the layers which are adjacent to the surface layer. The states with lowest energy will then extend into the vacuum, where the effective potential is more attractive. The same argument explains why all bulk interlayer states are found at higher energies than the surface state. According to our results, the energy gap between surface and bulk states is ~ 0.3 eV.

The bulk interlayer band has a width of 0.38 Ry, i.e., much larger than that of a free electron (0.25 Ry). Such strong dispersion originates from the nonlocality of the effective model potential, which in turn is due to the different orthogonality conditions with respect to σ- and π-valence states. As a result, symmetric states (e.g., Γ states) sample on the average a more attractive potential than antisymmetric states (e.g., A states). This nonlocality

affects the bandwidth considerably. In fact, under the assumption of a local orthogonality potential equal to U^{+}_{orth}, the bandwidth reduces to 0.04 Ry.

Finally, it should be mentioned that the electronic states of the highly dispersed band have been interpreted[4] as Block combinations of empty $3s$ carbon orbitals. This interpretation, however, is in contradiction with the symmetry of our wave function at the A point. We find that the bulk state at A is odd under the reflection σ_h with respect to the atomic planes. It is impossible to construct such a state from a linear combination of atomic $3s$ orbitals, since the latter are even under σ_h.

Summarizing, we have predicted the existence and have investigated the origin of surface states in a layered material, graphite. Unoccupied surface states are associated with the presence of a strongly dispersed interlayer band, whose width originates from the nonlocality of orthogonalization effects. The absence of orthogonality outside the surface plane leads to the formation of a surface state at lower energy. These findings provide a consistent interpretation of the data of Fauster *et al.*[1] Surface states derived from interlayer bands could exist in other layered materials, their energies being controlled by the interlayer spacing and the strength of orthogonalization effects.

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[a]Also at Istituto di Fisica Teorica and Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Richerche, Università di Trieste, I-34014 Trieste, Italy.

[b]Permanent address: Institut fur Physikalische Chemie, University of Vienna, A-1090 Vienna, Austria.

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