Prediction of Electronic Interlayer States in Graphite and Reinterpretation of Alkali Bands in Graphite Intercalation Compounds

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The existence of a new kind of electron state in graphite and in alkali graphite intercalation compounds is predicted with use of self-consistent local-density all-electron theory. These interlayer states, which exhibit free-electron character parallel to the layers, form a band close to the Fermi energy and provide for alkali graphite intercalation compounds a new understanding of the origin of bands previously interpreted incorrectly as arising from alkali s electrons.

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Experimental and theoretical studies of pure graphite and alkali-metal graphite intercalation compounds (AGIC) have provided the following commonly accepted description of their valence energy-band structures.[1] (i) In graphite the sequence of bands with increasing energy is σ and π bonding, π and σ antibonding, with the Fermi energy, E_F, in the middle of the π bands. (ii) In AGIC's, an additional strongly dispersed band is present close to E_F. It is called the "alkali band" since it is thought to arise from alkali s electrons. In LiC_6 its bottom is ~1.7 eV above E_F while in KC_8 its location relative to E_F has not yet been established.[1] We show here that the generally accepted energy-band structure of graphite is incomplete above E_F and that the interpretation of the "alkali band" in AGIC's is incorrect. We find that the AGIC "additional" band is actually an interlayer free-electron band which preexists above E_F in pure graphite.

We have studied three model two-dimensional systems: (i) a Li layer sandwiched between two graphite layers (C_6-Li-C_6 system) with the same crystallographic arrangement as in bulk LiC_6, (ii) the same system but without the alkali atoms (C_6-C_6 system) for several interlayer distances, and (iii) a graphite monolayer (C_6). Electronic energies and wave functions were obtained with the all-electron local-density full-potential self-consistent linearized augmented plane-wave (FLAPW) method for thin films.[2]

The C_6-Li-C_6 system has D_{6h} symmetry and its unit cell contains twelve C atoms and one Li atom. Its band structure at the Γ point [Fig. 1(a)] is consistent with existing energy bands for LiC_6.[3] The levels below E_F correspond to the σ and π bonding states of graphite. Because of the presence of two C_6 layers, these levels appear as pairs of states, one symmetric and one antisymmetric with respect to the Li plane. The energy separations are larger for π states than for σ states. Let us consider the Γ_1^+-Γ_2^- pair of empty states found just below vacuum level.[4] Their charge densities are given in Figs. 2(a) and 2(b). The Γ_2^- state [Fig. 2(a)], which is located 3.2 eV above E_F, has 97% of its charge in the vacuum region. It corresponds to a surface state of

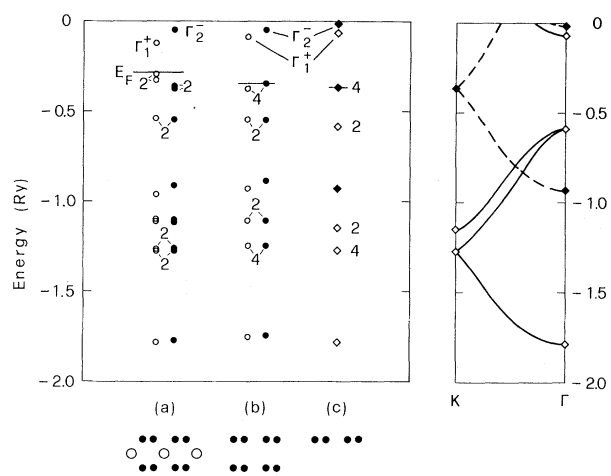

FIG. 1. Band eigenvalues at Γ for (a) C_6-Li-C_6, (b) C_6-C_6, and (c) C_6 monolayer. Open (solid) symbols represent symmetric (antisymmetric) states with respect to z-reflection symmetry. Numbers give the degeneracy of the levels. The Fermi energies are indicated by horizontal lines. Crystallographic structures are schematically given at the bottom. The energy bands for a graphite monolayer along the Γ-K direction are given at the right side.

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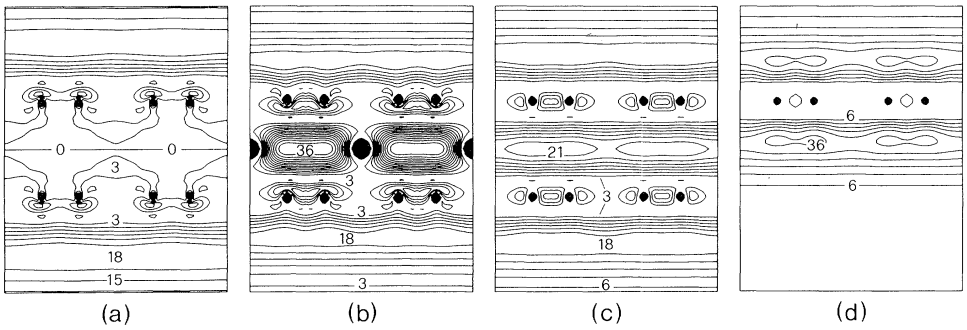

FIG. 2. Charge-density contour plots for the Γ_2^- state of (a) C_6-Li-C_6 and the Γ_1^+ state of (b) C_6-Li-C_6, (c) C_6-C_6, and (d) C_6. Contours are given at multiples of 3×10^{-3} electron/Å^3 in (a), (b), and (c), and of 6×10^{-3} electron/Å^3 in (d).

a LiC_6 crystal with finite thickness and has not been found in bulk calculations. The Γ_1^+ state is located 2.2 eV above E_F, in agreement with the absolute energy of the bottom of the "Li band" of bulk LiC_6.[5] 38% of its charge is in between the two graphite layers [Fig. 2(b)].

The amount of interlayer charge of the Γ_1^+ state is rather low for a state supposed to originate from Li 2*s* orbitals. Furthermore, this charge is strongly nonspherical around the Li atoms [the *s*-like charge is less than 1% within the Li augmented plane wave (APW) sphere with radius 1.36 a.u.]. We have therefore inspected the logarithmic derivative of the *s* radial solution within the Li APW sphere and found that the Li 2*s* orbital actually gives rise to a resonance at higher energy, above vacuum zero. This high-energy location of Li 2*s* states is not surprising if one considers that the average radius of the Li 2*s* orbital (3.9 a.u.) is about half the carbon interlayer distance (3.5 a.u.). Hence, the orthogonality repulsion with lower-lying σ and π graphitic states will raise considerably the energy of Li 2*s* states and will also reduce their localization. Preliminary FLAPW studies of a C_8-K-C_8 sandwich yielded similar results. The K orbitals give rise to a resonance just above vacuum zero,[6] while the Γ_1^+ state is at lower energy, just below E_F. These results show that the nature of the Γ_1^+ state close to E_F in C_8-Li-C_6 and C_8-K-C_8 is more complex than the generally accepted picture of a predominantly alkali valence state.

As a decisive test, we removed the Li atoms from C_6-Li-C_6, keeping the carbon sites unchanged, and studied the resulting system consisting of two graphite layers with *AA* stacking. Its unit cell contains four C atoms, but in order to make the comparison with C_6-Li-C_6 easier, we consider the three-times-larger unit cell corresponding to a C_6-C_6 double layer. The backfolded energies at Γ [Fig. 1(b)] are very similar to those of the C_6-Li-C_6 sandwich, apart from the fact that some splittings have disappeared because of the higher translational symmetry. The two bands above E_F are still there. Hence their existence is independent of the Li atoms. The Γ_1^+ state now lies somewhat higher in energy than in C_6-Li-C_6. Its charge density [Fig. 2(c)] shows that it is an interlayer state which is not localized to the carbon atoms but which exhibits free-electron character in the planes parallel to the layers.

A question arises concerning the bonding character of the state in the direction perpendicular to the layers. Is the electron confined between the two layers, or is it already bound to a single graphite layer? We have therefore computed the band structure of a graphite monolayer, keeping the in-plane lattice parameter unchanged. Again, for an easier comparison with C_6-Li-C_6, we consider a C_6 monolayer whose backfolded energies at Γ are displayed in Fig. 1(c). The bound state is seen to exist for a single graphite layer. Its charge density [Fig. 2(d)] shows again that it is not localized to the C atoms but is rather bound to the neutral graphite monolayer by its attractive short-range potential. Since the potential extends symmetrically from the layer, two states are actually bound to C_6, one symmetric and one antisymmetric. The Γ_1^+ interlayer state found for C_6-C_6 is the bonding combination between the two Γ_1^+ single-layer states. The Γ_2^- state of C_6-C_6 (which becomes a surface state when the slab thickness is increased) is simply the antibonding partner of the same Γ_1^+ single-layer states. The antisymmetric state bound to the C_6 monolayer

gives rise to resonances of the C_6-C_6 system.

We have also carried out one-dimensional model calculations which show that the bonding and antibonding interlayer states found in C_6-C_6 and C_6-Li-C_6 depend on the strength of the planar averaged attractive electrostatic potential V [Fig. 3(a)] of the graphite layer, and on the distance d between carbon planes, but not on the crystallographic structure of the system. Both the electrostatic potential energy of an electron added to one graphite layer and orthogonality repulsions are described through effective potentials U^+ and U^- for symmetric and antisymmetric states, respectively [Fig. 3(a)]. U^+ and U^- only depend on the electron distance to the layer and are adjusted to fit the Γ_1^+ and Γ_2^- FLAPW energies and wave functions in C_6. These effective potentials are then used to study the higher bound states of a C_6-C_6 system with arbitrary interlayer distance d. Interlayer polarization effects (i.e., self-consistent readjustment of the layer potentials at large distances) are taken into account by inhibiting superposition of the individual layer potentials. The resulting eigenvalues versus d are given in Fig. 3(b), together with FLAPW results for C_6-C_6 computed for the d values found in pure graphite (d_1), LiC_6 (d_2), and KC_8 (d_3). Agreement is satisfactory, apart from some discrepancies at d_3 due to our approximation of the polarization effects. The percentage of interlayer charge for the lowest Γ_1^+ state is very sensitive to the interlayer distance. It increases from 23 (17) in pure graphite to 35 (27) in LiC_6 and 67 (63) in KC_8 for the FLAPW (model) calculations.

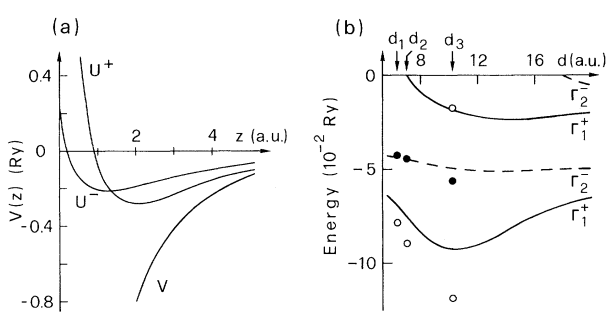

FIG. 3. (a) The planar averaged first-principles electrostatic potential V of a C_6 monolayer, together with the effective potentials U^+ (symmetric) and U^- (antisymmetric). (b) Interlayer states at Γ for C_6-C_6, as functions of the interlayer distance d. Full (dashed) lines and open (full) circles represent symmetric (antisymmetric) eigenvalues of the model and the FLAPW calculation, respectively. Note the greatly expanded energy scale relative to that of Fig. 1.

The results of Fig. 3 indicate that interlayer states also exist at the d value of pure graphite regardless of the particular layer stacking. We therefore predict the existence in graphite of a previously unrecognized band in the range of energies of the π antibonding states. Apparently such an interlayer band could not be detected in previous linear combination of atomic orbitals (LCAO) band-structure calculations since they were based only on $2s$ and $2p$ carbon orbitals.[7] We find this band to be clearly present (but not interpreted) in the band structures obtained by pseudopotential[8] and cellular[9] methods. This band has apparently also escaped definite experimental detection. The main reason is that the relevant states are confined to the interlayer region and therefore have small overlap with various kinds of filled levels which are initial states for excitation processes (i.e., $1s$ C states for x-ray absorption and σ and π bonding states for uv reflectivity measurements). In addition, dipole selection rules forbid transitions to this interlayer band at several points of the Brillouin zone. However, its existence might be confirmed in experiments which involve transitions to the band from the diffuse conduction states at higher energy, e.g., bremsstrahlung isochromat spectroscopy measurements.[10]

The results presented here demonstrate that (i) a new kind of state is present in pure graphite just above E_F. It originates from interlayer bonding states which exhibit free-electron character in the planes parallel to the layers. (ii) The so-called "Li band" in LiC_6 actually originates from interlayer bonding electron states orthogonalized to the Li $1s$ core [see Fig. 2(b)]. The occurrence of this band is not correlated to the presence of the Li atoms. (iii) The Li $2s$ valence orbitals give rise in LiC_6 to electron states located at higher energy than those resulting from the interlayer bonding states in agreement with earlier LCAO results.[7] (iv) Conclusions similar to (ii) and (iii) also apply to K-intercalated graphite.

Finally, we lay stress on the fact that the existence of interlayer states is not restricted a priori to AGIC's. They might occur in other types of GIC's, as well as in other layered compounds, provided that the layers are sufficiently electronegative.

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Localization in One-Dimensional Disordered Systems in the Presence of an Electric Field

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The influence of an electric field F on the nature of electronic states in a one-dimensional disordered Kronig-Penney model is studied. By study of the Poincaré map of the Kronig-Penney model in a field, the transmission coefficient T was calculated as a function of system size L. T is found to behave as $L^{-\alpha(F)}$, with $\alpha \sim 1/F$, for small F which indicates power-law localization. In this regime, it is predicted that the resistance $R(F) \simeq R(0)(1-b|F|)$, which may be checked experimentally.

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The question of localization of the eigenstates in one dimensional (1D) disordered systems has been extensively studied both numerically and analytically.[1] It is by now well established that in a 1D model all eigenstates are localized regardless of the amount of disorder.[2] Experiments on quasi one-dimensional disordered metallic systems (thin wires) are in qualitative agreement with localization theory.[3] While much work has been done for the study of the energy spectrum of an electron in a finite or semi-infinite periodic lattice in the presence of an electric field,[4] very little is known for the problem of a 1D disordered system in an electric field,[5,6] especially regarding the nature of the localized states.

It is the purpose of this Letter to examine the size dependence of the transmission coefficient T in a 1D disordered system when an electric field F is present. The study of the transmission coefficient has been used successfully to analyze the nature of the electronic states.[7-10] The model studied in this paper is

$$\left[-\frac{d^2}{dx^2}+\sum_{n=1}^{L} b_n \delta(x-n) - Fx\right]\psi(x) = E\psi(x), \qquad (1)$$

where b_n is the strength of the nth δ-function potential, taken to be a random variable with rectangular probability distribution of width W. Here F is the product of the electric field by the electron charge e. The numerical study of Eq. (1) can be simplified if we use the Poincaré map representation of the Schrödinger equation. This consists in relating the wave-function amplitudes at different lattice sites. Specifically, defining

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