PHYSICAL REVIEW B VOLUME 46, NUMBER 8 15 AUGUST 1992-II

Tight-binding density of electronic states of pregraphitic carbon

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(Received 4 November 1991; revised manuscript received 21 January 1992)

The density of states of pregraphitic (disordered) carbon has been investigated using a *tight-binding* description of the electronic structure. The *tight-binding* Hamiltonian has been diagonalized using the recursion method for different stackings of graphene layers. The density of states of π electrons in a disordered stacking usually called "turbostratic" graphite and the resulting behavior near the Fermi level are compared to the results obtained for the Bernal structure, for the rhombohedral structure, and for the simple hexagonal structure.

I. INTRODUCTION

Graphite is a prototype of layered crystal with strong covalent bonds within the two-dimensional hexagonal layers and much weaker bonds (van der Waals interactions) between the layers. At a carbon sp^2 site, three of the four valence electrons are assigned to the trigonally directed sp^2 hybrids which form σ bonds; the fourth electron lies in a p_z orbital normal to the σ bonding plane. These p_z orbitals form weak π bonds with adjacent p_z orbitals. It follows that the basic features of the electronic structure[1,2] of graphite can qualitatively be understood in a single-layer approximation.[3] The weak interaction between successive lattice planes only introduces small splittings and shift for the π and the π^* bands.

Quantitatively, the electronic properties of graphite(s) depend on the way the graphitic planes are stacked on each other. In the Bernal structure,[4] the layers of hexagonally arranged carbon atoms are alternately stacked (*ABABAB* pattern). It is the common structure of graphite, but natural (and synthesized) graphite is found to contain small amounts of rhombohedral graphite, where the layers are stacked in an *ABCABC* fashion. Moreover, in different stages of Li intercalated graphite, a new periodic modification has been observed:[5] the carbon atoms are directly located on top of each other, leading to an *AAAAAA* stacking. This last configuration has not been detected in pure graphite.

Tight-binding electronic models exist for these three different structures of graphite: the Slonczewski-Weiss-McClure (SWMcC) model for the Bernal graphite,[1] the Haering-McClure model for the rhombohedral graphite,[6] and a recent study of the simple hexagonal graphite.[7]

The pregraphitic form of carbon studied in this work, called "turbostratic" graphite, is a peculiar stacking of parallel graphitic monolayers with no periodicity along the *c* axis (axis perpendicular to the graphitic layers).[8] The graphitic layers are shifted and rotated at random and the interlayer spacing is changing from plane to plane. The irregularities and the nonperiodicity of such a stacking must lead to a "fuzziness" of bottoms and tops of the electronic band edges, like in other forms of amorphous carbon.[9]

In the present work, the turbostratic graphite has been considered as a real nonperiodic material, and the different types of interactions between p_z carbon orbitals have been parametrized using the values deduced from *ab initio* calculations for two periodic models of graphite: the Bernal structure[1] and the simple hexagonal graphite,[7] where the electronic structures have already been computed around the Fermi level.[2,10,11]

This work is aimed at producing realistic determinations of the density of states at the Fermi level that allow comparative studies among the four allotropic structures of graphite (*AAA* hypothetical stacking, Bernal structure, rhombohedral, and turbostratic graphite). In principle, these densities should be very much alike because they are all mainly dominated by the two-dimensional in-plane interactions. This is indeed true except for the immediate vicinity of the Fermi level (ε_F) where the four structures differ significantly from each other. This energy region around ε_F is of particular interest since it governs most of the electronic and transport properties of these materials.

II. THEORETICAL METHOD

The calculation of the density of states of noncrystalline solids requires special techniques that do not exploit translational invariance. The technique applied in the present work is the recursion method which leads to a continued-fraction expansion of the Green's function.[12] When applied to a *tight-binding* Hamiltonian, this method is a powerful tool for computing the local spin-orbital density of states of valence electron bands in disordered systems.

An amorphous cluster of turbostratic graphite, required by the recursion algorithm, has been created by stacking graphitic planes (with the usual honeycomb bidimensional lattice) with random rotations and translations generated as follows (Fig. 1). When adding a new graphene layer to the stack, the plane is translated in the horizontal directions with equal probabilities by zero, one or two C-C stretching vector of the underlying two-dimensional (2D) lattice. In addition, the plane is rotated by an arbitrary angle selected at random with a uniform distribution in the interval $[0,\pi/3]$.

To compare the electronic properties of turbostratic arrangement with those of crystalline modifications of graphite, the same technique has also been applied to *AAA* stacking, *ABAB* stacking, and *ABC* stacking using clusters generated along the same way, except that there are no rotations whereas the translations are periodic with the following sequences: 0,0,0,... for *AAA*; 0,1,0,1,... for *ABAB*, and 0,1,2,0,... for *ABC*.

The *tight-binding* interaction parameters between carbon p_z orbitals are adapted from simple hexagonal graphite (see below). The distance between layers in our disordered cluster is kept constant and equal to 3.335 Å which is the interlayer spacing obtained by total-energy minimization for simple hexagonal graphite.[11] In the actual turbostratic material, this average interlayer spacing is greater and varies between 3.354 and 3.44 Å,[13] depending on the high-temperature treatment.

The Hamiltonian used is that of Slater and Koster,[14] in the two-center approximation for the hopping parameters. As the present interest resides in the π electronic bands, we only consider a single p_z orbital per carbon atom. The different types of hopping interactions between p_z carbon orbitals in turbostratic graphite have been categorized as "horizontal," "vertical," and "sloping" ones (Fig. 2). The "horizontal" interactions (β_0) connect first-neighbor atoms within the same graphitic plane. The "vertical" interactions are established between an atom *I* and those atoms *J* which lie inside the circle of radius r_0, centered at the uprightness of the atom *I*, in the neighboring (β_1) or next-neighboring graphitic planes (β_2 or β_5, depending on whether the circle r_0 in the first-neighboring plane is free of an atom or not). The "sloping" interactions are settled for those atoms *J* in the first-neighboring planes which are positioned outside the circle of radius r_0 but inside a circle of radius r_1 (β_3 or β_4, depending on whether the circle r_0 is empty or not). The constraints imposed to the radii r_0 and r_1 are the following (Fig. 3): the circle of radius r_0 does not contain more than one atom; the circle of radius r_1 does not contain more than six atoms; if the circle of radius r_0 contains an atom, its three first neighbors must be inside the circle of radius r_1 but the six second neighbors must be outside. The values that we have retained and which satisfy these constraints are $r_0=0.36$ and $r_1=1.37$ in unit of the first-neighbor C-C distance.

The numerical parametrization of these β_i interactions has been adapted from *ab initio* values of similar interactions met in crystalline forms of graphite: the set of parameters α_i for the simple hexagonal graphite[7,11] completed by the γ_i parameters of SWMcC model for the Bernal structure.[1,2] The *ab initio* values of the β_i interactions used for turbostratic and rhombohedral graphites, are found to be $\beta_0=3.16$ eV,[15] $\beta_1=0.36$ eV,[11] $\beta_2=-0.02$ eV,[2] $\beta_3=0.32$ eV,[2] $\beta_4=-0.03$ eV,[11] and $\beta_5=0.013$ eV.[11]

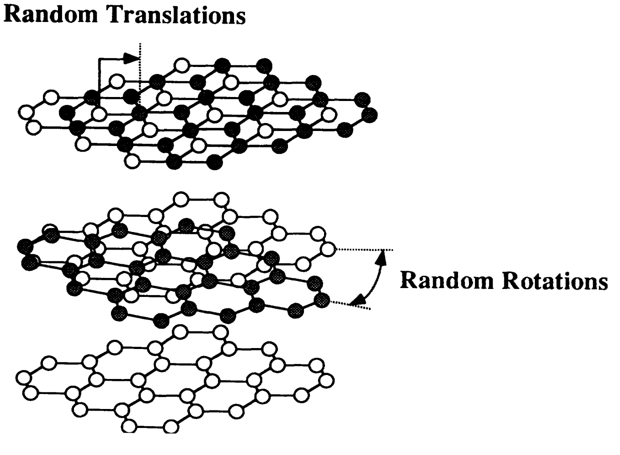

FIG. 1. Representation of the operations imposed to the graphitic planes in the construction of the atomic cluster of turbostratic graphite (see text). In the example illustrated here, the translation of the graphitic layer is by one C-C vector.

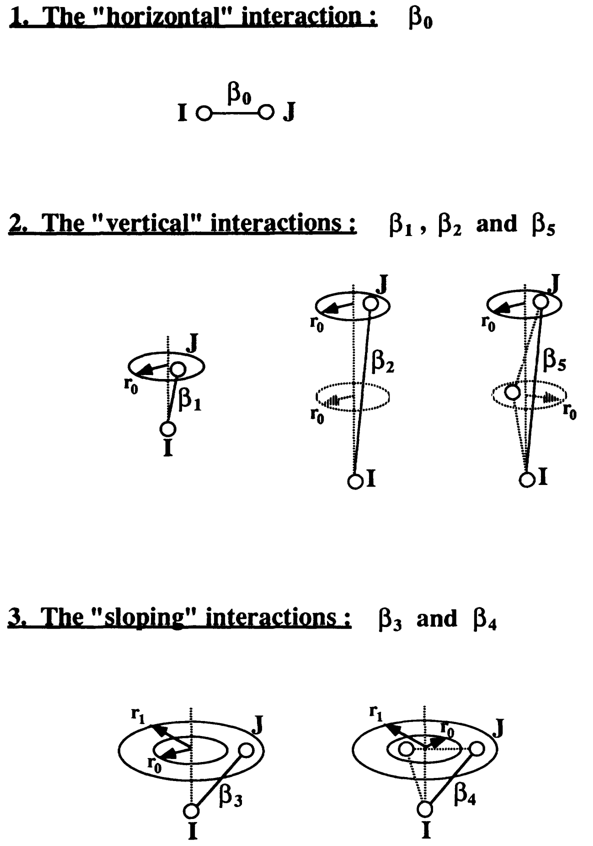

FIG. 2. Representation of the six different types of interactions between two atoms (labeled *I* and *J*) in turbostratic graphite.

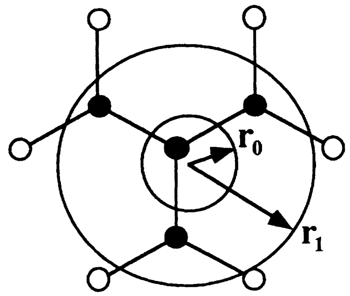

FIG. 3. Illustration of the r_0 and r_1 circles used to discriminate the various C-C interactions (see text).

III. DENSITIES OF STATES

The clusters used in this study contain 35 736 carbon atoms distributed in 24 graphitic layers. The recursion technique has been applied with periodic boundary conditions in the vertical direction. The size of each graphitic layer (1489 atoms) in the stacking has been selected on the basis of the number of recursion coefficients needed to obtain a good accuracy on the local density of states. In the present calculations, 30 levels of continued fraction (60 coefficients) have been computed. A special technique has been used to extrapolate the continued fraction to a much higher number of levels (200–400) in order to construct the densities of states displayed below.[16]

Calculations have been carried out for the three periodic graphites and for turbostratic graphite. Applications of recursion technique to turbostratic graphite require averaging configurational-dependent densities of states. Here, this process has been performed by averaging the power moments of the densities of states, deduced from the continued-fraction expansions. From the average moments, a continued-fraction expansion has been developed for the averaged density of states, using extended-precision arithmetic to circumvent numerical instabilities.

The density of states of *AAA* hypothetical stacking is presented in Fig. 4. In this case, the Fermi level lies 0.019 eV above the average of the p_z atomic level, which has been chosen as the zero of energy. The value of the density of states at the Fermi level, $n(\varepsilon_F)$, is 0.0085 states/eV atom per spin.

The density of states of Bernal structure is shown in Fig. 5 (top); the position of the Fermi level is 0.0 eV and $n(\varepsilon_F)$ is 0.0033 states/eV atom per spin. These two first values for the densities of states at the Fermi level are in good agreement with *ab initio* calculations.[7] The contribution of the two different kinds of atoms in the *ABABAB* stacking has also been investigated in this study. The *A* atoms have a near-neighbor atom in the plane directly above or below. By contrast, *B* atoms have no near-neighbor atoms in the adjacent plane. The two partial densities of states are also presented in Fig. 5 (bottom). The density of states of *B* atoms is 0.0056 to be compared with 0.0011 for *A* type. This is related to the well-known SWMcC band structure around the Fermi level (also shown in Fig. 5). The arithmetic average of these two partial densities of states leads to the 0.0033 value of the *ABABAB* density of states.

The density of states of rhombohedral graphite is presented in Fig. 6. In this case, the Fermi level again coincides with the position of the p_z orbital ($\varepsilon_F = 0$) and the value of the density of states (DOS) per spin at the Fermi level is 0.0021 states/eV atom. This value is greater than the preceding estimation of McClure[17] who considers the *ABCABC* DOS to be inside the following interval: $[0.85\times10^{-4}; 1.95\times10^{-4}]$ states/atom eV spin.

Finally, Fig. 7 shows the density of states of turbostratic graphite which has been averaged over 2400 independent configurations generated on the computer. For this purpose, 24 partial densities of states have been computed on the central atom of each of the 24 graphitic layers that compose our 35 736-atom cluster and the calculation has been repeated 100 times. Here (Fig. 7), the position of the Fermi level has been shifted to a higher energy ($\varepsilon_F = 0.11$ eV); $n(\varepsilon_F)$ is now 0.0034 states per atom eV

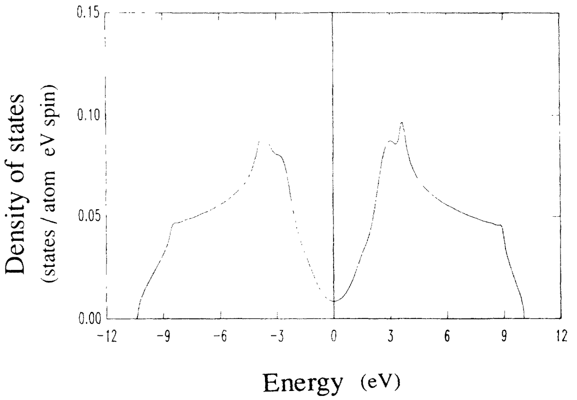

FIG. 4. Partial density of states of π electrons in simple hexagonal graphite.

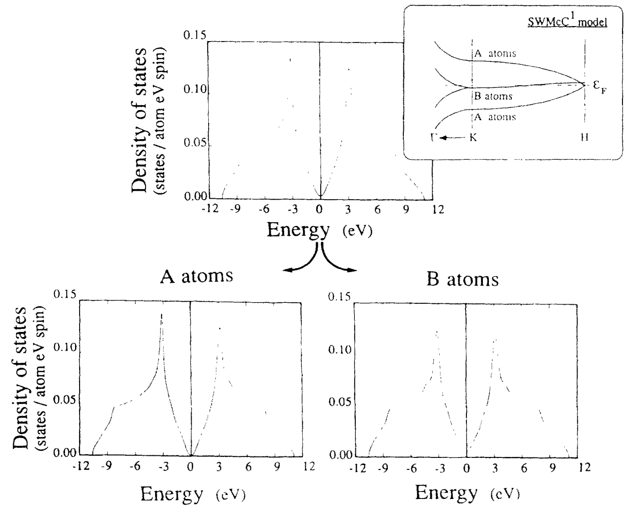

FIG. 5. π-electron density of states of hexagonal graphite and the well-known model of SWMcC for the band structure between K and H, around the Fermi level (top). Projections of the π electronic distribution of states on the unequivalent A and B sites (bottom).

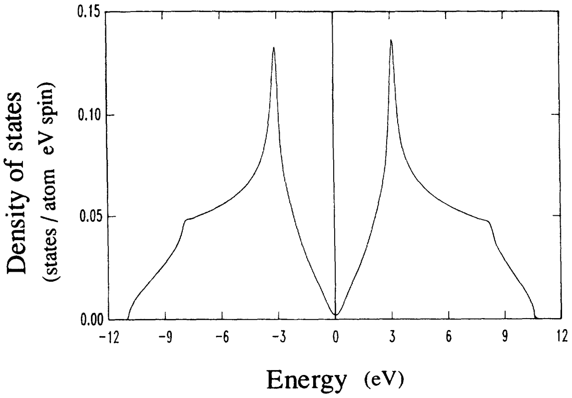

FIG. 6. Density of states for π electrons in rhombohedral graphite.

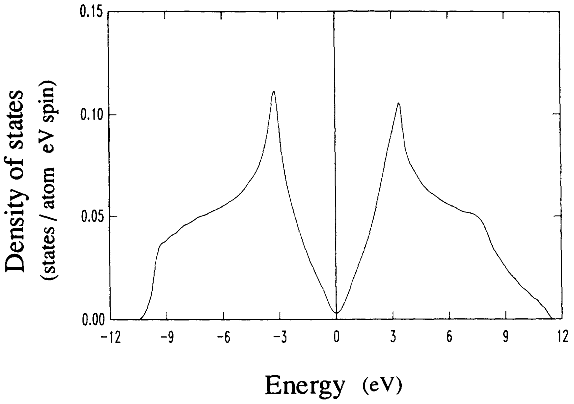

FIG. 7. Density of π electronic states of turbostratic graphite averaged over 2400 configurations.

per spin, a value which is found to be very close to that of *ABABAB* case.

At the band edges, the densities of states of three crystalline graphites suddenly increase from zero to a nearly constant value, exhibiting a clear characteristic of a two-dimensional behavior (Figs. 4–6). The density of states obtained for turbostratic graphite (Fig. 7) also clearly presents this 2D behavior, a little less pronounced.

IV. CONCLUSION

In spite of the fact that graphites are predominantly two-dimensional materials, the weak interlayer interaction plays an important role in determining the π-electron structure near ε_F, the region dominating transport and low-energy excitation properties. We have indeed shown that various graphite periodic and nonperiodic modifications possess different values of the density of states near ε_F due to the different interlayer stacking order. The nonperiodic case of turbostratic graphite is found to be very close to natural graphite (*ABAB* stacking) both in shape and in value for the densities of states around the Fermi level.

In this study, emphasis was put on the effects brought about by a model of stacking disorder on the electronic properties of turbostratic graphite which was therefore viewed as an "ideal" nonperiodic cluster while actual turbostratic samples also contain impurities, dislocations, grain boundaries, random interlayer spacing, etc. This real disorder which cannot be taken into account in this calculation greatly affects the transport properties.

ACKNOWLEDGMENTS

We thank V. Bayot, L. Piraux, J.-P. Issi, X. Gonze, A. Lucas, J.-P. Vigneron, and A. Moore for their interest in this work. Two of the authors (J.-C. and Ph.L.) have benefited from the financial support of the National Fund for Scientific Research (Belgium). This paper presents research results of the Belgian Program on Interuniversity Attraction Poles initiated by the Belgian State–Prime Minister's Office–Science Policy Programming. We also acknowledge the use of the IBM-3090 of the Calculation Center of Louvain-La-Neuve and the Namur Scientific Computing Facility (Namur-SCF), which are common projects between IBM Belgium and, respectively, the Catholic University of Louvain-La-Neuve (UCL) and the Facultés Universitaires Notre-Dame de la Paix (FUNDP).

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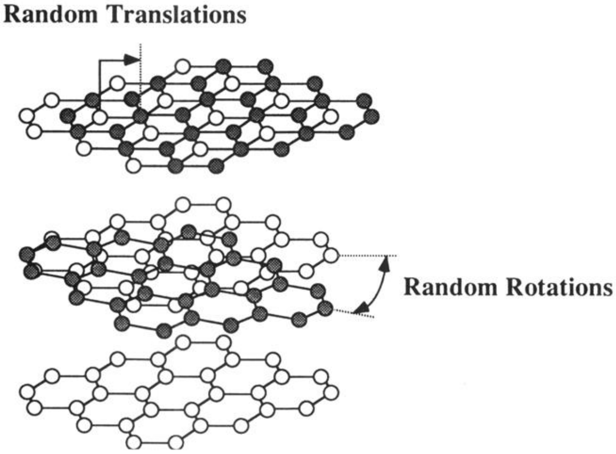

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