Electronic Structure of Superhoneycomb Systems: A Peculiar Realization of Semimetal/Semiconductor Classes and Ferromagnetism

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Lateral superstructures with honeycomb symmetry are shown to be classified, with a simple criterion, into semimetals with gapless k-linear dispersions, semiconductors, and metals. In some of the classes, the symmetry enforces flat bands to exist, which implies the occurrence of ferromagnetism when the electron correlation is turned on. These provide a unique opportunity for band structure engineering.

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Although recent advances in fabricating superlattices or such molecules as fullerenes [1,2] have made us realize that exotic structures provide an intriguing playing ground for condensed-matter physics, the lateral superstructures with superperiod along two-dimensional (2D) directions have yet to be fully explored. A most important question is whether there exist any unusual band-theoretical or electron-correlation effects due to the lateral superperiod, since the usually conceived effect is only the predictable appearance of band gaps at minizone boundaries. In this context the honeycomb symmetry is of distinct interest, since one can ask how the anomalous semimetallic (k-linear) band structure in its simplest form (graphite) will persist for superhoneycomb structures. The massless (k-linear) mode is intriguing, since this appears in, e.g., the parity anomaly in the quantum Hall effect [3]. In the present Letter we show that superstructures with honeycomb symmetry are classified, with a simple criterion, into classes which encompass all semiconducting, semimetallic and metallic cases. Hence the honeycomb symmetry implies massless dispersion under a certain condition, but not always. More remarkably, *dispersionless* (flat) bands appear systematically, which implies a ferromagnetism when the electron-electron repulsion is considered.

An initial motivation for our looking into superhoneycomb systems came from an organic material called azite [unit cell $=(C_{27}N_3H_6)_2$, inset of Fig. 1] [4,5], which is roughly a graphite sheet with periodic ($\sim$15 Å) perforations (or an atomistic "antidot array") and has been reported by Chapman to be synthesized as a by-product in an attempt to fabricate fullerene. We can also envisage such a molecular network as a "2D zeolite": When some molecules such as halogens [5] are doped, the property of the host is important in considering doped materials, with possibly some charge transfers as in the case of graphite intercalation compounds.

We start with the band structure of azite obtained with discrete variational-X_α-linear combination of atomic orbitals (DV-Xα-LCAO) method [6] assuming for simplicity that all the C-C and C-N bond lengths are equal to 1.39 Å, a value intermediate between the single and double bond lengths of carbon, and the C-H to be 1.09 Å. The result (Fig. 1) shows that the system is a semiconductor with a direct gap at the K point. The wave functions in the highest occupied band have the character mainly of π orbitals of C and N atoms.

We can in fact give a general criterion for characterizing the band structure of all the honeycomb superstructures from group-theoretical considerations, where we concentrate on the tight-binding model to single out the π bands. Curiously, the classification involves not only the global symmetry but also the atomic configuration within the unit cell.

Consider superstructures of honeycomb symmetry, where the atomic structure within the hexagonal cell is arbitrary with either D_6 (space group $P6mm$) or lower C_6 symmetry (space group $P6$). The honeycomb symmetry *forces* us to regard the unit cell as comprising two "superatoms," α and β, each of which has an identical atomic configuration with C_3 symmetry (see the insets of

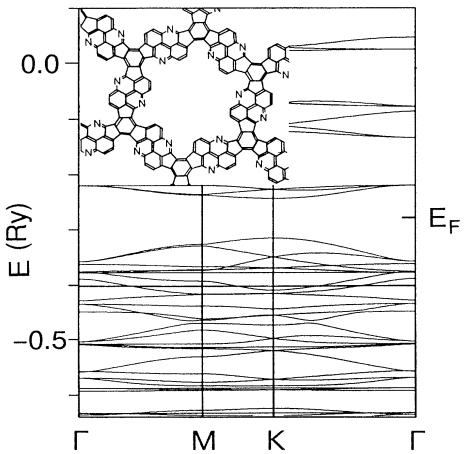

FIG. 1. Band structure of azite. The inset depicts the structure of azite after Ref. [5].

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TABLE I. The case of odd numbers of A or E representations are marked along with the band structure, which is semiconducting (sc), semimetallic (sm), or metallic (m).

Type	Formula unit	Γ	K	Bipartite	Nonbipartite
A_0	$(C_{3m})_2$			sc$+n(\geq 0)$ flat band(s)	sc$(n=0)$/m
A_C	$(C_{3m+1})_2$		E	sm$+n(\geq 0)$ flat band(s)	sm$(n=0)$/m
B_0	$(C_{3m+3/2})_2$	A,E	A,E	sc$+n(\geq 3)$ flat bands	m
B_C	$(C_{3m+5/2})_2$	A,E	A	sm$+n(\geq 1)$ flat band(s)	m

Figs. 2 and 3). To be compatible with honeycomb (C_6) symmetry, it follows that each superatom has a threefold axis at the center and a twofold axis on the boundary. Although the assignment of superatoms may not be unique, we can distinguish case A in which we can make neighboring α and β share no atoms and case B in which they have to share an atom at the boundary.

Since there is a threefold axis at each corner of the hexagonal cell (i.e., at the center of each superatom), the number of atoms within each superatom is $3m$ in case A and $3(m+\frac{1}{2})$ in case B, where m is an integer. There may be an additional atom (threefold axis) at the corner of the hexagonal cell, so that we can further classify type A into type A_0 with no corner atoms with a unit cell $=(C_{3m})_2$ and A_C with corner atoms, $(C_{3m+1})_2$, and type B into type B_0 $(C_{3(m+1/2)})_2$ [7], and B_C, $(C_{3(m+1/2)+1})_2$. Now the classification is complete.

Theorem I: For a superhoneycomb system with one orbital (one π orbital for carbon) per atom, the number of one-dimensional irreducible representations (which we symbolically call A) and that of two-dimensional irreducible representations (E) at the K point (with threefold symmetry) and the Γ point (with sixfold symmetry) in the Brillouin zone (BZ) are related with the type of the structure. Table I lists those structures with an odd number of A representations or E representations at the K and Γ points.

We can prove this theorem by recombining atomic orbitals into ϕ_s,ϕ_x,ϕ_y with s,x,y symmetries, respectively, for superatoms α and β (as well as for the boundary atoms for type B) to enumerate the irreducible representations. The distinction between the cases with and without corner atoms comes from the fact that an E representation arises at K from the s orbital for each of those sites, a situation specific to honeycomb systems [8].

The table shows that the number of representations is *odd* for E states at the K point in a type-A_C system, etc. If the lattice is bipartite, these odd number of A or E states lie symmetrically about the orbital energy (taken as the origin of energy), so that E and A states with $E=0$ must exist. Hence the π band to which the E state belongs forms a zero gap (with a k-linear dispersion as confirmed from the $\mathbf{k}\cdot\mathbf{p}$ perturbation) at these points. This implies that, for the half-filled band (with one electron per atom) for which $E_F=0$, any type-A_C or -B_C system should be semimetallic. On the other hand, the π band to which the $E=0$ A state belongs in type B_0 or B_C is completely flat in the whole BZ (see theorem II below). The remaining type A_0 is semiconducting (unless there is an accidental degeneracy in the zone interior). Since the k-linear mode in type A_C becomes massive, thereby making the system semiconducting when the corner atoms are removed, the electronic structure is not determined by the size and orientation of the unit cell alone unlike the situation in carbon nanotubes [9].

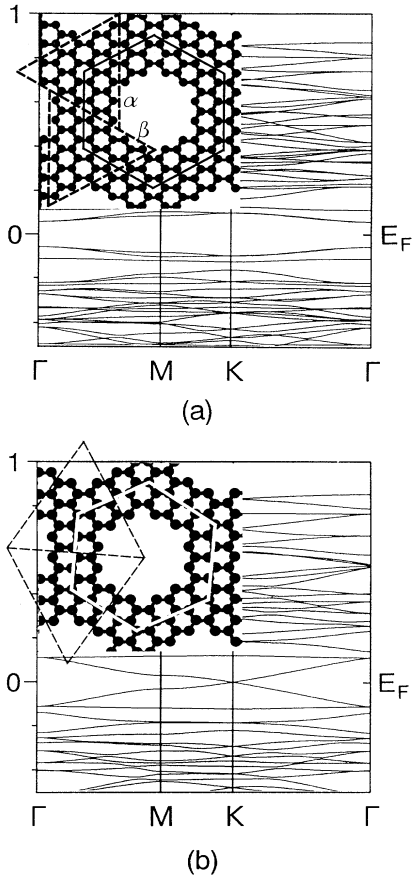

FIG. 2. Band structures of a type-A_0 superhoneycomb system, $(C_{3m})_2$ with $m=12$ (a) and a type-A_C system, $(C_{3m+1})_2$ with $m=8$ (b). The position of E_F in the case of the half-filled band is $E=0$. The insets depict the atomic structure, on which the nearest-neighbor transfers are considered with $t=-0.3$ Ry to fit the band structure of graphite. The unit cell comprising superatoms α and β (adjacent triangles) is indicated with dashed lines, while we also indicate the hexagonal unit.

Examples of type-A_0 and -A_C systems realized as long-period graphites are shown in Fig. 2. There a difference between A_0 and A_C is confirmed in terms of the band folding: The K point of the original graphite is folded onto Γ in type A_0, while K is folded onto K in type A_C. The tight-binding band structure (Fig. 2), which is qualitatively similar to the DV-Xα-LCAO result, indeed endorses the above property.

We have quantitatively probed the effect of perforation for a series of systems with progressively larger holes with the size of the unit cell kept constant. The gap in type A_0 is a sensitive (roughly increasing) function of the size of the hole, while the k-linear dispersion in type A_C becomes flatter.

The completely flat bands have the following property:

Theorem II: For the tight-binding model on the bipartite lattice, there exist in general flat band(s) at $E=0$ ($=E_F$) whose degeneracy is $6l$ ($l \geq 0$ is an integer) for type $A_0, 6l \pm 2$ (A_C), $6l \pm 3$ (B_0), or $6l \pm 1$ (B_C), with type-A_0' or -A_C' systems excepted.

Here the primed type A denotes the case in which the superatoms α and β have the interchanged bipartite sublattices (which never occurs in type B). The number of flat bands coincides with the difference, $n_b - n_a$, in the numbers of a and b sublattice sites within a unit cell, and this is in fact a realization in honeycomb systems of Lieb's theorem [10], which asserts that the tight-binding band in a bipartite lattice must contain $(n_b - n_a)$ flat bands at $E=0$. Thus the honeycomb symmetry dictates the structure of both flat and dispersive bands in that a type-B_0 system has at least threefold degenerate flat bands (i.e., both the E band having $E=0$ at K and the A band are flat), while a B_C system has at least one flat band on top of the semimetallic bands.

Lieb was originally motivated to derive that, when the electron-electron (short-range) repulsion is introduced, the electron correlation makes the ground state of a half-filled system having flat band(s) ferromagnetic with a total spin of $S=N(n_b - n_a)/2$ [10], which can be interpreted as a generalized Hund's coupling within the flat bands [11]. Here N is the total number of unit cells. Thus the class of superstructure considered here opens up opportunities for ferromagnetism [12].

Lieb's theorem does not provide the wave functions in the $E=0$ flat bands or about the existence of flat bands with $E \neq 0$ [which are seen to exist in Fig. 3(a)]. Here the $E=0$ eigenfunctions, which are shown to be confined on b sites, are typically depicted for a B_0 system in Fig. 3 (for Γ; for general k point, we can only attach a phase). There the threefold degeneracy corresponds to the rotation of the amplitude by 0, $2\pi/3$, and $4\pi/3$. There, we can show that the "interband" matrix elements of the repulsion (the Hubbard U) are nonzero, which we can identify as the reason why all of the spins on the multiple flat bands are ferromagnetically coupled [11].

When the bipartite condition is relaxed by, e.g., intro-

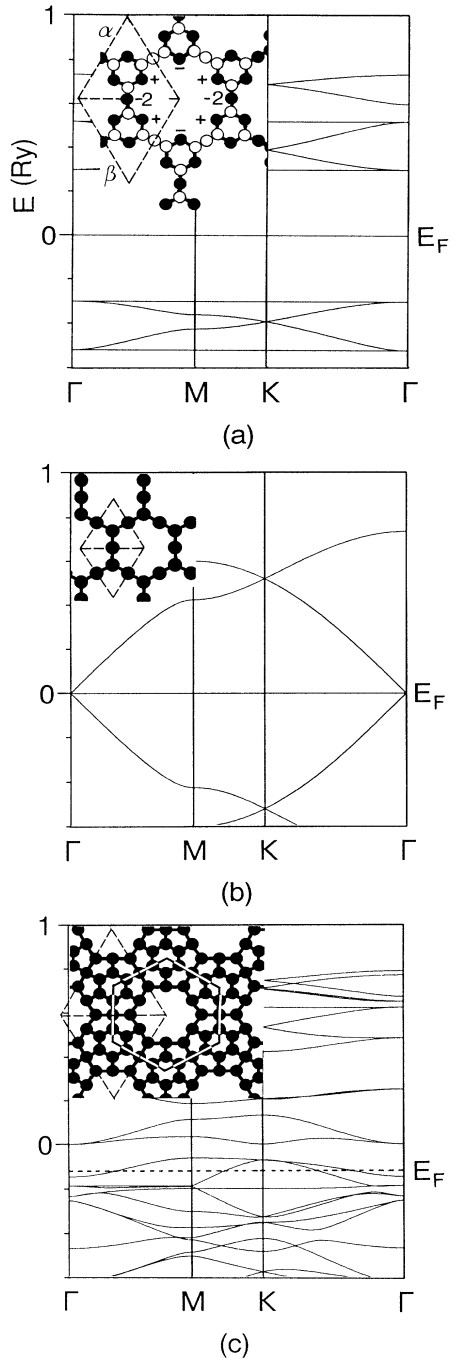

FIG. 3. Band structures of a type-B_0 system, $(C_{3m+3/2})_2$ with $m=2$ (a) and a type-B_C system, $(C_{3m+5/2})_2$ with $m=0$ (b). A band structure of the type-B_0 system for the nonbipartite case with five-membered rings, $(C_{3m+3/2})_2$ with $m=4$, is shown in (c). The degeneracy of the flat bands at $E=0$ is three (one) for B_0 (B_C), while the flat bands become dispersive for the nonbipartite case. The insets depict the atoms in the hexagonal unit cell, where an eigenstate belonging to one of the $E=0$ flat bands is indicated for Γ with amplitude 0 (open circle), ± 1 ($\pm$) in (a).

ducing odd-membered rings, the symmetry in the band structure will be degraded, but the semiconducting property in a type-A_0 system will remain, since theorem I still applies. Azite is a manifestation of this case (we have checked that the tight-binding band for the azite structure with all nitrogen atoms replaced with carbon atoms is similar to the DV-Xα result for the original azite). Similarly, a nonbipartite A_C system will remain the k-linear semimetal. For type-B systems or type-A systems with flat bands, on the other hand, a relaxation of the condition will make the flat bands dispersive, thereby inducing a semimetal-metal (or semiconductor-metal) transformation as confirmed in the numerical examples in Fig. 3 [13].

There is a long history for the group-theoretical study of the semimetallic properties of 2D graphite, notably by Lomer [14] or by Coulson [15]. One might be tempted to assume that the honeycomb symmetry implies semimetallic bands, but the present study shows that the situation is far richer.

We have thus unraveled an example that a lateral superstructure does indeed provide an intriguing band-structure engineering. Specifically, a systematic appearance of flat bands implies a spin ferromagnetism in, e.g., organic materials. In discussing aromatic compounds, Kekulé structures are often evoked. We notice that the condition for the existence of flat bands here is a sufficient condition for the absence of Kekulé structures. While the absence of Kekulé structures for finite molecules sometimes indicates an instability [16], the stability of infinite 2D systems will have to be checked from total-energy calculations. The lateral superstructures also will be interesting in terms of the orbital magnetism [17,18] or the superconductivity [19]. If we apply magnetic field, a broken time-reversal symmetry will cause a splitting of the degeneracy of the E representations, along with the quantum Hall effect and the Hofstadter butterfly for honeycomb systems [20].

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[8] In the other possible symmetry, i.e., square (C_4) superstructures, the system is either semiconducting for A_0 and A_C cases (unit cells $=C_{4m},C_{4m+1}$) with m even or k^2 zero-gap otherwise. Flat bands appear when two unit cells comprise two C_4-symmetry superatoms sharing an atom, where a B_0 (B_C) system has double (single) flat bands at $E=0$.
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