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Comment on Graphene Nanoflakes with Large Spin: Broken-Symmetry States

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In a recent Letter,[1] Wang, Meng, and Kaxiras (WMK) proposed a strategy for constructing graphene fragments (nanoflakes) with large electron spin magnetic moments originating from the topological frustration of π-bonds. The elementary building block of the proposed magnetic graphene nanoflakes is a triangular fragment with 3-fold symmetry and a net magnetic moment stemming from the unequal number of carbon atoms in the two sublattices of graphene. As an extension of this idea WMK also considered a 6-fold symmetric "Star of David" graphene nanoflake, Figure 1a, and fractals structures derived from it. The magnetic moments of the proposed structures were verified by first-principles electronic structure calculations.

In the present paper, we point out that a more thorough analysis of spin states reveals the existence of broken-symmetry configurations[2] with antiferromagnetic (AF) correlation of locally spin-polarized regions. Calculations of such AF states are not always trivial and require explicit spatial spin-symmetry breaking for the initial guess wavefunctions. Additional first-principles calculations using such a broken spin-symmetry initial wavefunction show that the AF configuration of the Star of David with zero net spin, Figure 1b, is more stable (by 0.087 eV) than the originally considered high-spin state. This result is in full agreement with the Lieb theorem,[3] which predicts zero total spin for graphene nanoflakes with equal number of atoms in the two sublattices. Similar conclusions have been drawn for hexagonal graphene fragments[4] of the same symmetry. The $S = 0$ configuration of this nanoflake naturally fulfills the preferred AF coupling between nearest neighbor atoms,[5,6] which is also true for fractal structures derived from it.

Here, we propose a modified strategy for generating fractal structures with large spin based on a building block consisting of a spin-polarized triangular fragment, the same as in the WMK proposal. Figure 2a shows such a fragment with total spin $S_0 = (N_A - N_B)/2$ with N_A, N_B the numbers of atoms in sublattices A and B. Larger structures can be generated according to the Sierpinski sieve construction (fractal dimension $d = \log_2 3 \approx 1.58$) as shown in Figure 2b,c for fractal levels $q = 2$ and 4. In this case, no switch of the sublattice where the majority spin resides is required, the number of atoms in sublattice A dominates globally for all fractal structures and as a result the large spin state is favored. The total spin increases with the fractal level q as $S_q = S_0 3^q$ in accordance with the arguments presented by WMK. The results of our first-principles electronic structure calculations for $q = 1$, 2 are in full agreement with the predicted total spins of the ground state configurations.

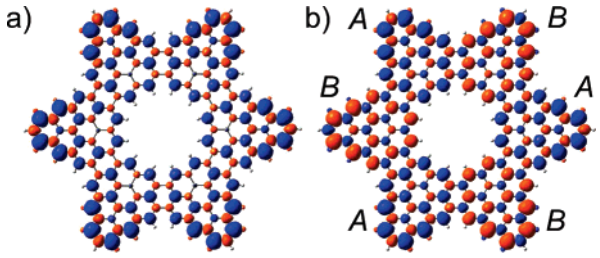

Figure 1. Two spin configurations of the "Star of David" structure: (a) $S = 3$; (b) $S = 0$, antiferromagnetic, broken-symmetry ground state. Positive (blue) and negative (red) spin density isosurfaces are shown and regions with dominating A and B sublattice sites are marked.

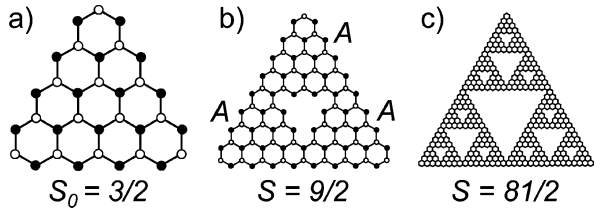

Figure 2. Sierpinski sieve fractal structures of graphene nanoflakes with corresponding total spin S: (a) elementary triangular building block; (b) $q = 2$ and (c) $q = 4$ fractal structures. The two sublattice sites are shown as open and filled circles; the sublattice A sites dominate globally.

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