

Stability of the ferromagnetic state in a mixed sp^2 - sp^3 carbon system

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(Received 5 May 2009; revised manuscript received 13 August 2009; published 14 September 2009)

In the search for an all-carbon structure that is ferromagnetic at room temperature, Ovchinnikov *et al.* [J. Mol. Struct. THEOCHEM **251**, 133 (1991); *ibid.* **251**, 141 (1991)] identified a possible candidate in a crystal with both sp^2 and sp^3 hybridization by means of *ab initio* calculations on its fragments. We have examined the structural and magnetic stability of this system in its crystalline form using hybrid density functional theory. It is found that the system is structurally unstable with respect to a previously discovered, spinless carbon polymorph. Also, the present periodic calculations show that the approach based on the examination of the magnetic properties of fragments is misleading when used to predict long-range electronic and spin interactions in this class of materials.

DOI: [10.1103/PhysRevB.80.104415](https://doi.org/10.1103/PhysRevB.80.104415)

PACS number(s): 75.20.Ck, 75.30.-m, 75.50.Xx, 71.15.Mb

I. INTRODUCTION

In recent years a number of experiments have provided increasing evidence of room temperature ferromagnetism in carbon compounds. Proton bombardment of graphite induces a ferromagnetic state in the damaged sample³ which x-ray circular dichroism measurements⁴ have shown to originate exclusively from carbon sp electrons. Magnetic hysteresis was also observed in organic polymers prepared by H enriched pyrolysis⁵ and also upon implantation of N and C in nanosized diamond particles.⁶

If the magnetic ground state is the result of local moments present at defects, then it is essential to establish which defects actually occur and to determine the mechanism underpinning their long-range magnetic coupling. As the experimental characterization of the magnetic phase is problematic, theoretical calculations have an important role to play in determining possible local geometries. A number of previous theoretical studies have addressed the origins of magnetism in nonplanar⁷ and planar carbon systems.⁸⁻¹⁴ The coexistence of sp^2 and sp^3 bonded C atoms has also been considered as a possible origin of magnetism in C structures. In the case of graphitic ribbons, for instance, the presence of mono- and dihydrogenated edges gives rise to a ferrimagnetic polarization of the graphitic π electron system.¹⁵

The quest for a carbon-based ferromagnet has occupied theoreticians for many years. Nearly 20 years ago, a ferromagnetic carbon structure with mixed sp^2 and sp^3 hybridizations was predicted by Ovchinnikov *et al.* who used a molecular mechanics approach combined with *ab initio* calculations.^{1,2} Due to the presence of unpaired electrons at the sp^2 bonded atoms, Ovchinnikov *et al.* found this structure to be ferromagnetic, with a magnetization density which, surprisingly, was predicted to be higher than that of pure iron. These predictions have been and still are very influential in the area of magnetism in organic materials¹⁶⁻¹⁹ and particularly in the very active area of research on graphite.^{3,20-22}

Here, results of hybrid density functional calculations on the crystalline structure proposed by Ovchinnikov *et al.* are

presented. This structure is found to be unstable and undergoes a barrier free transition to a known, spinless sp^3 hybridized network. In addition, it is pointed out that the fragment approach used in the work by Ovchinnikov *et al.* to determine the ferromagnetic nature of the crystal only assesses the likelihood of formation of local magnetic moments and leads to erroneous conclusions when addressing long-range interactions in this type of system.

II. COMPUTATIONAL DETAILS

The first-principles calculations presented here have been performed using the hybrid exchange density functional B3LYP (Refs. 23-25) as implemented in the CRYSTAL06 package.²⁶ Several of the calculations were repeated with the PBE functional²⁷ in order to assess the dependence of the predictions on the description of electronic exchange and correlation functional. Hartree-Fock (HF) calculations were performed for comparison with previous work. In CRYSTAL, the crystalline wave functions are expanded as a linear combination of atom centered Gaussian orbitals (LCAO) with s , p , d , or f symmetry. The calculations reported here are all-electron, i.e., with no shape approximation to the ionic potential or electron charge density. The all-carbon structure considered was found by Ovchinnikov *et al.*¹ with a molecular mechanics approach based on a force field method, and is shown in Fig. 1. The unit cell is orthorhombic with $a = 2.608 \text{ \AA}$, $b = 3.961 \text{ \AA}$, $c = 5.289 \text{ \AA}$, and contains an equal number of sp^2 and sp^3 bonded C atoms, with each sp^2 atom surrounded by sp^3 atoms only. Our geometry optimizations are performed using the algorithm proposed by Schlegel *et al.*²⁸ with a starting geometry identical to the structure of Ref. 1. Basis sets of double valence quality (6-31G* for C and 6-31G* for H) are used. These basis sets are adapted for periodic calculations starting from Pople's molecular basis sets.²⁹ A reciprocal space sampling on a Monkhorst-Pack grid of shrinking factor equal to 6 is adopted which results in 112 k points in the irreducible Brillouin zone and is sufficient to converge the total energy to within 10^{-4} eV per unit cell. The Gaussian overlap criteria which control the truncation of

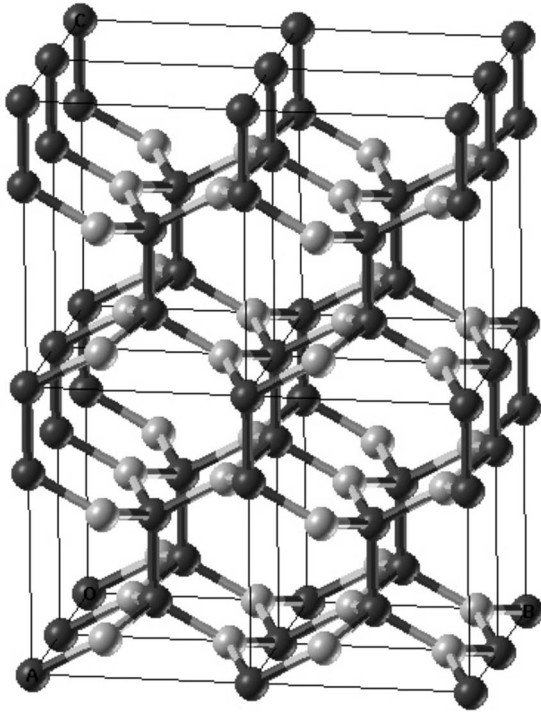


FIG. 1. All-carbon structure reported by Ovchinnikov *et al.* (Ref. 1). Gray and black spheres represent sp^2 and sp^3 atoms, respectively. The lines delimit the primitive unit cells.

the Coulomb and exchange series in direct space are set to 10^{-7} , 10^{-7} , 10^{-7} , 10^{-7} , and 10^{-14} . Typically linear mixing of 70% and an Anderson second order mixing scheme are used to guide the convergence of the self-consistent field procedure. The details of these numerical approximations can be found elsewhere.²⁶

III. RESULTS AND DISCUSSION

Calculations on the structure proposed by Ovchinnikov *et al.* (Fig. 1) and starting from initial states with broken spin symmetry lead to the spin-polarized solution shown in Fig. 2. The sp^2 atoms carry a magnetic moment of $0.30\mu_B$ while a smaller moment of $0.10\mu_B$ is found on the sp^3 atoms (not resolved in Fig. 2). In the state shown in the figure, the coupling between the magnetic moments located on the sp^2 atoms is antiferromagnetic. No ferromagnetic state is found to be stable within B3LYP for the crystalline structure proposed by Ovchinnikov *et al.* When the starting spin configuration is chosen to be ferromagnetic, the final, self-consistent solution is spinless. Remarkably, the energy of this spinless state is less than 1 meV above the energy of the antiferromagnetic state. Given the accuracy of current density-functional calculations, it is not possible to resolve the energetic ordering between these two states. This result indicates that, within B3LYP, the energy scale associated with kinetic delocalization (which favors the spinless solution) and that of the exchange interactions (which favors the spin-polarized antiferromagnetic solution) are of the same order of magnitude. This is consistent with the fact that, within a mean field model where on-site correlations are considered in a tight

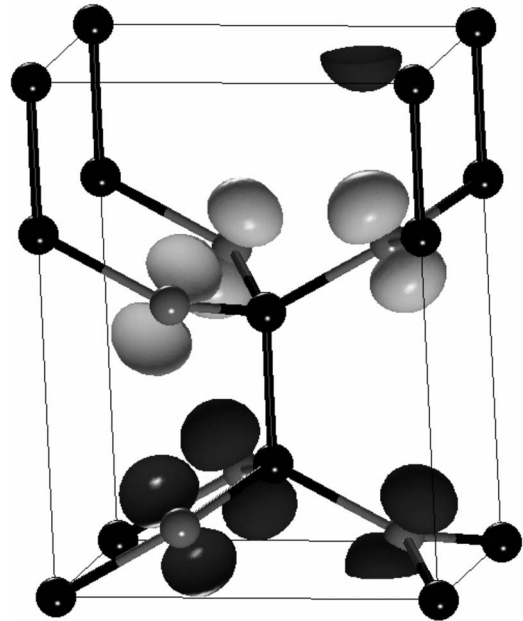


FIG. 2. Spin density for the antiferromagnetic state computed for the structure reported in Ref. 1. Gray and black spheres represent the sp^2 and sp^3 C atoms, respectively. Gray and black lobes represent the electronic spin up and spin down densities, respectively, with isosurface values of $\pm 0.015\mu_B/\text{\AA}^3$. The line delimits the primitive unit cell.

binding picture, t/U is close to 1 for organic magnets,³⁰ as opposed to transition metal magnets where it is close to 0.1.³¹ This is an important consideration when addressing the apparent mismatch between our predictions and those made in Refs. 1 and 2.

Due to limited computing power and software at the time, Ovchinnikov *et al.* performed calculations of the magnetic interactions on fragments only. All six pairs of sp^2 atoms separated by two bonds were found to prefer a triplet ground state. Of the eight pairs of radicals separated by three bonds, only one was found to favor the singlet state over the triplet state. These results were then extrapolated to the crystal as a whole and it was concluded that the overall exchange coupling in the three-dimensional structure would give rise to a ferromagnetic ordering with a predicted transition temperature higher than that of iron. This fragment-based approach may be appropriate for transition metal magnets where t/U is small³¹ but not for organic magnets where electron delocalization involves atoms beyond nearest neighbors and long-range effects are not negligible.^{8,30}

TABLE I. Singlet-triplet splitting energies (eV) for three different geometries of the fragment C4H8.

Geometry	HF ^a	HF ^b	MP4 ^a	B3LYP ^b
3	0.837	0.835	-0.911	-0.941
4	4.595	4.608	1.099	1.765
5	3.863	3.847	0.527	1.097

^aReference 2.

^bThe current work.

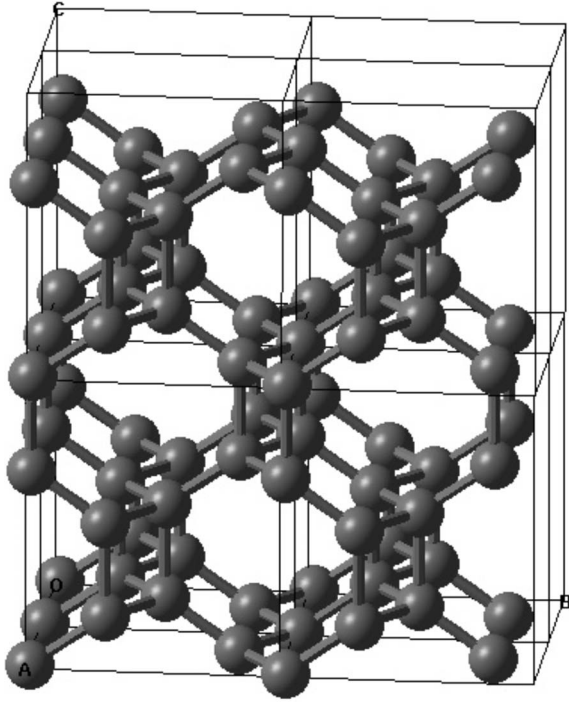


FIG. 3. Stable structure obtained by relaxing the structure in Fig. 1 reported in Ref. 1. The spheres represent the C atoms, all sp^3 hybridized. The lines delimit the primitive unit cells.

We have repeated some of the calculations on the molecular fragments, extracted at fixed geometry from the crystal and labeled 3, 4, 5 in Table II of Ref. 2. The HF and B3LYP outcomes are presented in Table I and compared with the results of Table II in Ref. 2 for the 6-31G* basis set. For these molecular fragments the HF results obtained in this work agree with the previous HF calculations, with the slight deviations to be ascribed to differences in the basis set. Interestingly, the B3LYP functional reproduces the trend found previously using fourth-order perturbation theory (MP4).

To test the dependence of our results for the crystal on the choice of the exchange-correlation functional, calculations were carried out within the generalized gradient approximation PBE. Both antiferro- and ferromagnetic arrangements of spins were found to be unstable with respect to the wholly spinless state. The qualitative difference in the predictions given by PBE and those of B3LYP are ascribable to the larger charge delocalization predicted by PBE due to the self-interaction error.³²

Full structural relaxation starting from the structure proposed by Ovchinnikov *et al.* was performed both with the B3LYP and the PBE functionals. Both functionals predict that this structure does not correspond to a minimum in the energy landscape of the atomic coordinates. In both cases the structural relaxation results in the equilibrium structure illustrated in Fig. 3. This structure has been recently predicted by Strong *et al.*³³ using density functional, PBE calculations and is spinless. The comparison of Figs. 1 and 3 demonstrates

TABLE II. Lattice parameters (in Å) for Ovchinnikov's structure (Ref. 1) and the stable structure obtained in this work after relaxation with B3LYP.

	a	b	c
Ref. 1	2.608	3.961	5.289
This work	2.553	4.215	4.938

that the sp^2 atoms in the structure proposed by Ovchinnikov *et al.* have paired in singlet states by forming σ bonds along the c axis (i.e., the vertical axis in the figures). The transition between these structures is barrier free and so the structure proposed by Ovchinnikov *et al.* is found to be unstable at all temperatures. Table II reports the lattice parameters of the two structures. The b axis expands while the c axis contracts due to the formation of the new bonds.

We also carried out a full structural optimization with the classical interatomic potential developed by Brenner³⁴ as implemented in the GULP code.³⁵ This is an environment-sensitive potential where C atoms can form and break different types of hybridized bonds. We find that the structure predicted by Ovchinnikov *et al.* is stable within this potential, with a slight readjustment of the lattice parameters compared to Ref. 1. Previous work has shown that the predictions of the Brenner potential agree with density-functional calculations only for carbon systems at low density.³⁶ The Brenner potential was developed for surfaces and molecules and in general for undercoordinated structures, and underestimates the tendency of C structures to convert from sp^2 to sp^3 bonding as their atomic density increases. The atomic density of Ovchinnikov's structure is about 2.9 g/cm³, which is close to the high density regime.³⁷

IV. CONCLUSION

The structural stability of a proposed ferromagnetic carbon polymorph predicted by Ovchinnikov *et al.*¹ was investigated within hybrid density-functional theory. The structure was found to be unstable with respect to sp^3 hybridization. The predicted equilibrium structure is spinless and fully sp^3 hybridized. The qualitative nature of this result is insensitive to the different treatments of electronic exchange and correlation used here. We also conclude that deducing the magnetic properties of crystalline materials from calculations of crystal fragments can lead to erroneous conclusions. The present calculations confirm that the Brenner potential underestimates the tendency to high coordination in carbon structures at high atomic densities.

ACKNOWLEDGMENTS

This work is supported by the European Union under the NEST FERROCARBON project (Grant No. CEC 012881). The authors acknowledge the use of the SCARF computing facilities at STFC.

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