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

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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 sample which x-ray circular dichroism measurements have shown to originate exclusively from carbon $sp$ electrons. Magnetic hysteresis was also observed in organic polymers prepared by H enriched pyrolysis and also upon implantation of N and C in nanosized diamond particles.

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 nonplanar and planar carbon systems. 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 $\pi$ electron system.

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. 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 materials and particularly in the very active area of research on graphite.

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. Several of the calculations were repeated with the PBE functional in order to assess the dependence of the predictions on the description of electron 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. with a molecular mechanics approach based on a force field method, and is shown in Fig. 1. The unit cell is orthorhombic with $a =2.608$ Å, $b =3.961$ Å, 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. 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. 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
the Coulomb and exchange series in direct space are set to
$10^{-7}$, $10^{-7}$, $10^{-7}$, 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 proce-
dure. The details of these numerical approximations can be
found elsewhere.\textsuperscript{26}

III. RESULTS AND DISCUSSION

Calculations on the structure proposed by Ovchinnikov \textit{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 pro-
posed by Ovchinnikov \textit{et al.} When the starting spin configu-
ration 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 antiferro-
magnetic state. Given the accuracy of current density-
functional calculations, it is not possible to resolve the ener-
getic 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 magni-
tude. This is consistent with the fact that, within a mean field
model where on-site correlations are considered in a tight
binding picture, $t/U$ is close to 1 for organic magnets,\textsuperscript{30} as
opposed to transition metal magnets where it is close to
0.1.\textsuperscript{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 \textit{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. Only one pair 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 cou-
ping in the three-dimensional structure would give rise to a
ferromagnetic ordering with a predicted transition tempera-
ture higher than that of iron. This fragment-based approach
may be appropriate for transition metal magnets where
$t/U$ is small\textsuperscript{31} but not for organic magnets where electron delocal-
ization involves atoms beyond nearest neighbors and long-
range effects are not negligible.\textsuperscript{8,30}

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

<table>
<thead>
<tr>
<th>Geometry</th>
<th>HF\textsuperscript{a}</th>
<th>HF\textsuperscript{b}</th>
<th>MP4\textsuperscript{a}</th>
<th>B3LYP\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.837</td>
<td>0.835</td>
<td>-0.911</td>
<td>-0.941</td>
</tr>
<tr>
<td>4</td>
<td>4.595</td>
<td>4.608</td>
<td>1.099</td>
<td>1.765</td>
</tr>
<tr>
<td>5</td>
<td>3.863</td>
<td>3.847</td>
<td>0.527</td>
<td>1.097</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reference 2.
\textsuperscript{b}The current work.
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 (GGA) 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.

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. using density functional, PBE calculations and is spinless. The comparison of Figs. 1 and 3 demonstrates that the sp² 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 Brenner as implemented in the GULP code. 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. 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 sp² to sp³ 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.

### IV. CONCLUSION

The structural stability of a proposed ferromagnetic carbon polymorph predicted by Ovchinnikov et al. was investigated within hybrid density-functional theory. The structure was found to be unstable with respect to sp³ hybridization. The predicted equilibrium structure is spinless and fully sp³ 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

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8 Corresponding author. barbara.montanari@stfc.ac.uk
29 See http://www.crystal.unito.it/Basis_Sets/carbon.html
37 The density of graphite is in the range 2.09–2.23 g/cm³ and that of diamond is about 3.5 g/cm³.