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Magnetic properties of polymerized C_{60}: The influence of defects and hydrogen

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A combination of reactive force field molecular dynamics and hybrid-exchange density functional theory (DFT) generates a defective structure of Rh-C_{60} possessing an inter-cage link. Hybrid-exchange DFT is used within periodic boundary conditions to investigate the long-range magnetic coupling between the resulting defects. Inelastic neutron scattering experiments highlight the presence of hydrogen chemically bonded to carbon in the magnetic samples. A simple spin model previously applied to studies of planar conjugated π electron systems is used to illustrate the mechanism through which chemically bonded hydrogen leads to a ferromagnetic ground state for this system.

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The recent observation of high temperature ferromagnetism in carbon materials is of great interest both as it introduces a class of potentially highly tunable materials for use in magnetic devices and because it presents a major challenge to our current understanding of magnetism. At elevated pressures and temperatures cubic C_{60} fullerenes form well ordered two-dimensional polymerized phases. Below 9 GPa three distinct phases occur, with orthorhombic, tetragonal (T) and rhombohedral (Rh) symmetries.[1] Further heating of these phases beyond ~900 K results in the collapse of the C_{60} cages and the formation of hard "graphitic" phases. The ferromagnetic phases occur close to this phase boundary.[2,3] A remarkably high Curie temperature (T_c) of ~500 K was reported in initial studies,[3] with recent data indicating an even higher T_c of ~820 K.[4] Magnetic force microscopy (MFM) measurements[5] and additional experimental evidence[3] imply that the magnetism is an intrinsic property of carbon and not due to metallic impurities such as iron.

The experimental characterization of the magnetic phases has proven difficult and currently the detailed atomic structure is not known. *In situ* x-ray diffraction measurements reveal a thermally activated process which converts the Rh phase (Fig. 1) into the highly disordered graphite-like phase, which displays very broad Bragg peaks.[6] The detailed structure of the magnetic phase cannot be determined from this data. Transmission electron microscopy (TEM) reveals an apparently well ordered crystalline structure in which the C_{60} cages are largely intact and still in a Rh-C_{60}-like arrangement.[2] MFM studies established that only ~30% of the material is magnetic with the magnetism occurring in well defined domains.[5]

As the 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 carbon systems. Tight-binding molecular dynamics and cluster *ab initio* calculations have recently been used to analyze a single C_{60} cage with a carbon vacancy.[7] Density functional theory (DFT) calculations have been used to examine a fullerene molecule during the transition to a nanotube segment via a series of Stone-Wales transformations[8] and a fragment with negative Gaussian curvature,[9] hybrid-exchange DFT theory has been used to study a C_{60} dimer formed by forcing two fullerene cages against each other,[10] and complete active space self-consistent field (CASSCF) calculations have been performed on an isolated C_{60} cage with hydrogen atoms replacing the nearby C_{60} balls.[11] In all studies local moment formation has been demonstrated. It is clear that there are a large number of local defect structures which will result in such local moments. However, this is insufficient to explain the observed ground state which requires ferromagnetic coupling between the local moments. Recently, for instance, it was shown that in the periodic version of the prototype defective structure of Rh-C_{60} proposed by Andriotis *et al.*,[7] where a carbon atom is removed from each C_{60} cage, the magnetic moments localized on each cage are not able to couple through the inter-cage bonds formed during the 2+2 cycloaddition polymerization reaction.[12] If the magnetic ground state is the result of local moments present at defects, then it is essential to estab-

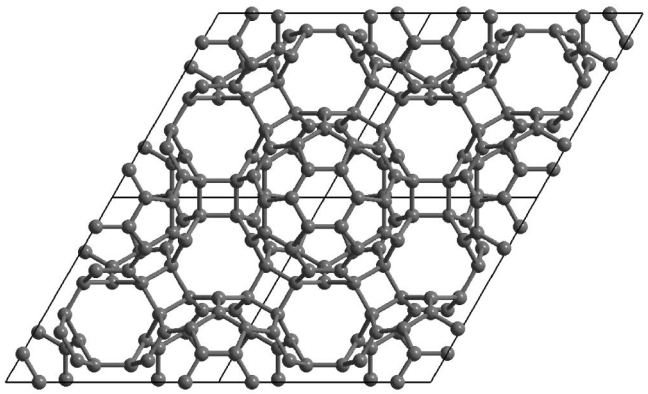

FIG. 1. The basal plane of the hexagonal cell of the perfect Rh-C_{60} structure.

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lish which defects actually occur and to determine the mechanism underpinning the long range magnetic coupling.

The present work represents the first theoretical investigation of the structural defects which occur spontaneously during the high pressure high temperature (HPHT) treatment of crystalline Rh-C_{60}. Calculations of the electronic structure within periodic boundary conditions allow the long-range magnetic coupling between the resulting defects to be investigated. Inelastic neutron scattering (INS) measurements are also performed which reveal the presence of hydrogen in the magnetic samples. The important role of hydrogen in determining the magnetic ground state of a common predicted defect structure is examined and rationalized with a simple model of the coupling mechanism.

The calculations were confined to a model system consisting of a single, two dimensional periodic, hexagonal layer of the Rh-C_{60} structure[1] described in (1×1) and (2×1) unit cells with no symmetry constraints. Reactive force field molecular dynamics (MD) at high pressures and temperatures is performed to produce defective structures. These simulations are carried out with the most recently developed variant of the bond order potential due to Brenner *et al.*[13,14] which models adequately bond breaking and formation processes. The MD calculations were performed within the NVT ensemble with a time step of 0.1 fs and run until equilibrium was reached. To explore potential defect structures, a large number of MD simulations were performed in which isotropic and anisotropic strains of between 4% and 6% were applied for temperatures in the range 800–1000 K.

The resulting defective structures are subsequently relaxed in hybrid-exchange DFT calculations. Hybrid-exchange DFT[15,16] has recently been shown to provide a significantly more accurate description of the ground state electronic structure and magnetic coupling in insulators than the generally used generalized gradient approximation.[17] Recent work on organic magnetic systems[12] indicates that the hybrid functional B3LYP is suitable for the current work.[15] A local orbital approach was adopted in which the crystalline orbitals were expanded in atom centered Gaussian basis sets of double valence quality (6–21 G^* for C and 6–31 G^* for H).[16] Reciprocal space sampling on a 2×2 Monkhorst-Pack grid[18] was sufficient to converge the total energies to $\sim10^{-2}$ eV per C_{60} cage. All structures were relaxed in the ferromagnetic configuration. By controlling the spin density of the *initial* density matrix, various other spin configurations were generated allowing intra- and inter-cage spin couplings to be determined.

An example of a common defect resulting from anisotropic strain is displayed in Fig. 2. In this structure a carbon atom is forced out of the "top" face of the cage, breaking bonds to the atoms labeled A and B in Fig. 2. The atom is displaced to position C and forms an additional inter-cage linkage. Analysis of the ground state spin density reveals local moments in the "dangling bonds" on atoms A, B, and C (Fig. 2). This defect is reminiscent of the vacancy-adatom pair, which is often seen in irradiated graphite,[19] and the structure appears to be a natural precursor to the decomposition of the polymerized fullerenes into the graphitic phase. All stable electronic configurations found for this structure show, however, that this system carries no net magnetization.

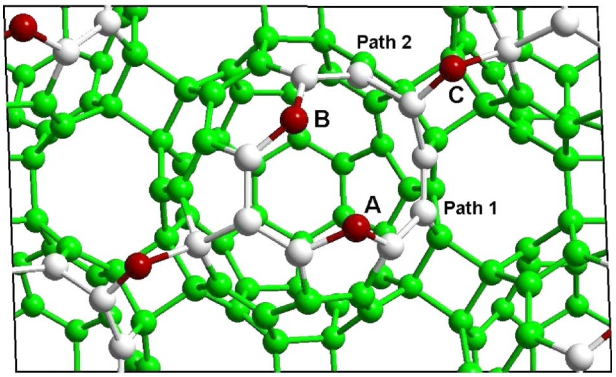

FIG. 2. (Color online) The open-cage defect structure. Atoms A, B, and C are undercoordinated, and the atoms shown in white are involved in two competing inter-cage coupling routes.

Several recent studies have looked at the role that hydrogen might play in magnetic carbon systems. For instance, the observed saturation magnetization of magnetic amorphous carbon is found to increase with the hydrogen concentration of the starting material.[20] In addition, the proton irradiation of highly orientated pyrolytic graphite induces intrinsic room temperature ferromagnetic ordering,[21] whereas a similar treatment with helium ions resulted in reduced magnetic signals. Previous DFT simulations have also shown that a graphene ribbon with both mono- and dihydrogenated zigzag edges exhibits a spontaneous magnetization[22] and tight-binding calculations have predicted spontaneous magnetization on the monohydrogenated zigzag edge of nanographite.[23] The involvement of hydrogen in the ferromagnetic behavior of Rh-C_{60} may provide an explanation for the disappearance of the magnetism upon annealing for several hours at a temperature below the destruction temperature of the C_{60} cages.[3]

In the current work, INS measurements have been performed in order to determine the hydrogen concentration in Rh-C_{60}. A 200 mg sample of Rh-C_{60}, confirmed to be ferromagnetic through Muon spin rotation and superconducting quantum interference device measurements, was analyzed in the MARI spectrometer at the ISIS pulsed neutron source.[24] MARI is a direct geometry chopper spectrometer with continuous detector coverage from 3° to 143°. A clear C-H stretch at 368 ± 1 meV and a broad C-C stretch at 170 ± 7 meV are present in the INS spectrum (Fig. 3), showing that a significant percentage of hydrogen covalently bonded to carbon is present in the ferromagnetic samples. To the authors' knowledge, this is the first observation of the presence of H bonded to C in the magnetic phase of Rh-C_{60}.

Potential sites for hydrogen intercalation in the structure shown in Fig. 2 were examined using hybrid-DFT calculations. The binding energies, calculated with respect to H_2 gas, for H at the low coordination sites, A, B, and C (see Fig. 2), were found to be 3.09, 2.91, and 2.45 eV, respectively. Hydrogen bonded to the A site is therefore preferred. With H bonded to this site, the ground state of the system is found to be *ferromagnetic* with a spin per C_{60} cage of 3.0 μ_B. The spin density map (Fig. 4) shows that the spin density is localized predominantly on the B and C sites while that at the A site is suppressed by the H.

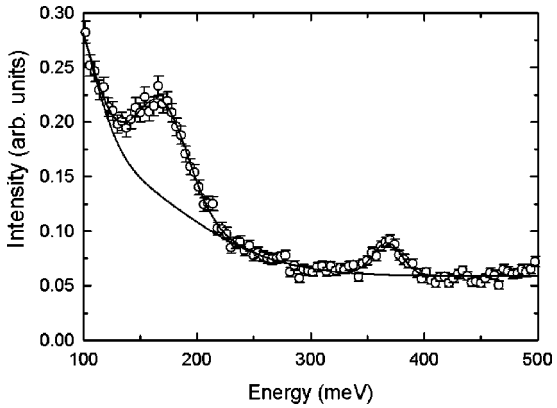

FIG. 3. The INS intensity, $S(E)$, with an incident energy of 600 meV. The sample was 99.8% purity C_{60}, converted to the magnetic Rh phase by quenching from 9 GPa and 800 K.

The magnetic interactions leading to this ground state can be understood in terms of a simple model that has been used previously to predict spin configurations in planar conjugated π hydrocarbon systems, such as organic radicals[25,26] and in extended bipartite lattices.[23,27] The model, based on the spin polarization effect,[26] requires that the spin direction alternates on neighboring atoms. This allows maximum spatial delocalization, and therefore stabilization, of unpaired electrons. The predicted ground state spin configurations of the open-cage fullerene structures and nanotube segments generated by Kim *et al.*,[8] all of the various defect structures generated by the simulation of HPHT treatment of Rh-C_{60},[28] and a recently prepared defect structure[7,12] are consistent with this simple model. This suggests that the model's range of applicability extends beyond planar systems. This model is therefore valuable in anticipating which defect structures will generate magnetic ground states in fullerene systems.

The model reveals the vital role played by hydrogen in the ferromagnetic coupling of the defect structure found here. Analysis of the defective structure without hydrogen shows that there are two competing pathways for inter-cage spin coupling. These pathways are highlighted in white in Fig. 2. The pathways lead to competing inter-cage magnetic interactions with path 1 generating antiferromagnetic coupling and path 2 ferromagnetic coupling. The coupling energies of these pathways are of similar magnitude leading to the net cancellation of inter-cage coupling and thus the overall ground state has no net magnetization. The bonding of hydrogen to atom A quenches the main spin center in path 1, leaving path 2 as the dominant inter-cage coupling mechanism and resulting in the ferromagnetic ground state.

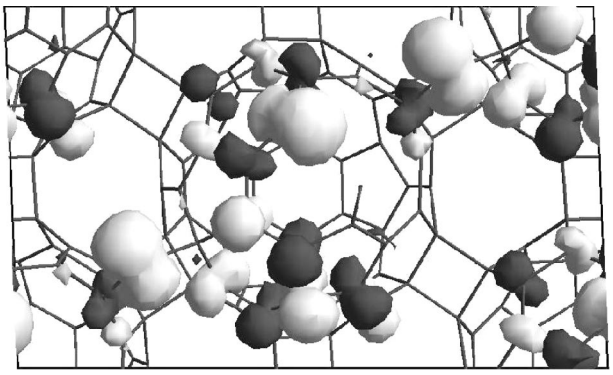

FIG. 4. The ferromagnetic ground state of the proposed structure with H bonded to atom A. The light isosurface of the spin density is of the value +0.008 μ_B, and the dark isosurface is of the value −0.003 μ_B.

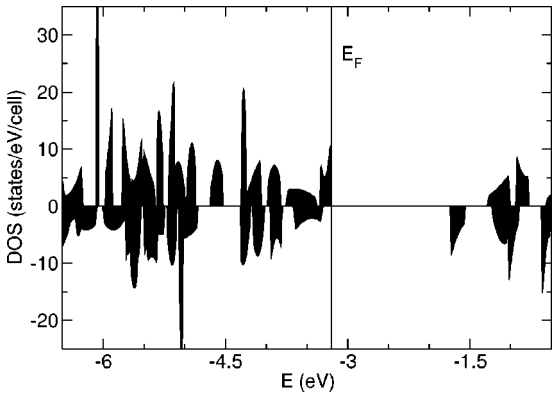

FIG. 5. The electronic density of the highest valence states and lowest conduction states for the ferromagnetic ground state of the proposed structure with H bonded to A. Positive and negative values of DOS refer to the spin-up and spin-down electronic populations, respectively. The vertical line indicates the Fermi energy, E_F.

The proposed structure retains essentially intact C_{60} balls within the rhombohedral symmetry as suggested by TEM.[2] In addition the average magnetization is measured to be 0.34 μ_B per cage.[2] For this to be the case ~11% of the C_{60} cages would be magnetic and the C_{60}:H ratio would also be ~11%. The C_{60}:H ratio can be estimated from the INS data. Fitting the data between 5 and 15 $Å^{-1}$ gives a C_{60}:H ratio of ~17% in excellent agreement with that predicted. A rough estimate of the extent of the magnetic phase can also be obtained from MFM images which yield ~30% in reasonable agreement with the INS and theoretical estimate.[5] The electronic density of states (DOS) for the ferromagnetic ground state, reported in Fig. 5, is typical of a spin polarized system and corresponds to a semiconducting ground state. The upper valence band edge is composed of majority spin states in a flatband composed of localized spin orbitals. The lower conduction band consists of minority spin states resulting in an indirect, spin-flip band gap of 1.44 eV. The smallest direct band gap between states of same spin is 1.74 eV. The inter-cage magnetic coupling can be determined by reversing the spin orientation on the nearby C_{60} cage. The computed energy difference between the ferromagnetic and antiferromagnetic states is 3 meV per cage. Although this energy difference is too small to explain room temperature ferromagnetism in Rh-C_{60}, the inter-cage linkage found does provide a mechanism for ferromagnetic coupling. It is possible that structures which allow greater spin delocalization or multiple linkages including interlayer linkages, will give rise to significantly larger inter-cage couplings.

In conclusion, reactive force field molecular dynamics simulations and hybrid DFT B3LYP calculations have lead to a defect structure for Rh-C_{60}. In this structure, long-range spin coupling, essential for the ferromagnetism, has been

considered explicitly through the investigation of an infinite, periodic system. The features which appear to favor the ferromagnetic ground state are the localization of spin density in a carbon vacancy, the formation of an inter-cage bridge structure (the inter-cage bonds of the ideal Rh-C_{60} structure are magnetically inert) and the quenching of an antiferromagnetic coupling pathway by chemically bonded H. The presence of intercalated H in a suitable concentration is confirmed by inelastic neutron scattering experiments. The magnetic structures resulting from this study can be understood in terms of a simple spin model previously applied to studies of planar conjugated π electron systems.

While the exact defect structure proposed here may not explain the room temperature ferromagnetism in carbon fullerene polymorphs, it is, to the authors' knowledge, the only structure considered so far that is obtained by simulating the experimental HPHT treatment that leads to the ferromagnetic phase, and is consistent with ferromagnetic inter-cage coupling which is essential to the observed magnetic ground state. The full characterization of the magnetic phase will require further experimental and theoretical work.

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[1] M. Núñez-Regueiro, L. Marques, J.-L. Hodeau, O. Béthoux, and M. Perroux, Phys. Rev. Lett. **74**, 278 (1995).
[2] R. A. Wood, M. H. Lewis, M. R. Lees, S. M. Bennington, M. G. Cain, and N. Kitamura, J. Phys.: Condens. Matter **14**, L385 (2002).
[3] T. L. Makarova, B. Sundqvist, R. Höhne, P. Esquinazi, Y. Kopelevich, P. Scharff, V. A. Davydov, L. S. Kashevarova, and A. V. Rakhmanina, Nature (London) **413**, 716 (2001).
[4] V. N. Narozhnyi, K.-H. Müller, D. Eckert, A. Teresiak, L. Dunsch, V. A . Davydov, L. S. Kashevarova, and A. V. Rakhmanina, Physica B **329**, 1217 (2003).
[5] K.-H. Han, D. Spemann, R. Höhne, A. Setzer, T. L. Makarova, P. Esquinazi, and T. Butz, Carbon **41**, 785 (2003); K.-H. Han, D. Spemann, R. Höhne, A. Setzer, T. L. Makarova, P. Esquinazi, and T. Butz, Carbon **41**, 2425 (2003).
[6] S. M. Bennington, N. Kitamura, M. H. Lewis, R. A. Wood, A. K. Fukumi, and K. Funakoshi, J. Phys.: Condens. Matter **12**, L451 (2000).
[7] A. N. Andriotis, M. Menon, R. M. Sheetz, and L. Chernozatonskii, Phys. Rev. Lett. **90**, 026801 (2003).
[8] Y.-H. Kim, J. Choi, K. J. Chang, and D. Tománek, Phys. Rev. B **68**, 125420 (2003).
[9] N. Park, M. Yoon, S. Berber, J. Ihm, E. Osawa, and D. Tománek, Phys. Rev. Lett. **91**, 237204 (2003).
[10] J. Ribas-Ariño and J. J. Novoa, Angew. Chem., Int. Ed. **43**, 577 (2004).
[11] J. Ribas-Ariño and J. J. Novoa, J. Phys. Chem. Solids **65**, 787 (2004).
[12] B. Montanari, J. A. Chan, W.-L. Chan, and N. M. Harrison, Mol. Phys. (to be published).
[13] D. W. Brenner, O. A. Shenderova, J. A. Harrison, S. J. Stuart, B. Ni, and S. B. Sinnott, J. Phys.: Condens. Matter **14**, 783 (2002).
[14] The GULP software as described in J. D. Gale, J. Chem. Soc., Faraday Trans. **93**, 629 (1997); J. D. Gale and A. L. Rohl, Mol. Simul. **29**, 291 (2003).
[15] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993); C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
[16] V. R. Saunders, R. Dovesi, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, N. M. Harrison, K. Doll, B. Civalleri, I. J. Bush, Ph. D'Arco, and M. Llunell, *CRYSTAL03 User's Manual* (University of Torino, Torino, 2003).
[17] I. P. R. Moreira, F. Illas, and R. L. Martin, Phys. Rev. B **65**, 155102 (2002); J. Muscat, A. Wander, and N. M. Harrison, Chem. Phys. Lett. **342**, 397 (2001); R. L. Martin and F. Illas, Phys. Rev. Lett. **79**, 1539 (1997); T. Bredow and A. R. Gerson, Phys. Rev. B **61**, 5194 (2000); J. K. Perry, J. Tahir-Kelhi, and W. A. Goddard, III, *ibid.* **63**, 144510 (2001); X. B. Feng and N. M. Harrison, *ibid.* **69**, 035114 (2004).
[18] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[19] F. Banhart, Rep. Prog. Phys. **62**, 1181 (1999).
[20] K. Murata, H. Ushijima, H. Ueda, and K. Kawaguchi, J. Chem. Soc., Chem. Commun. **18**, 1265 (1991); K. Murata, H. Ushijima, and H. Ueda, *ibid.* **7**, 567 (1992).
[21] P. Esquinazi, D. Spemann, R. Höhne, A. Setzer, K.-H. Han, and T. Butz, Phys. Rev. Lett. **91**, 227201 (2003).
[22] K. Kusakabe and M. Maruyama, Phys. Rev. B **67**, 092406 (2003).
[23] M. Fujita, K. Wakabayashi, K. Nakada, and K. Kusakabe, J. Phys. Soc. Jpn. **65**, 1920 (1996).
[24] www.isis.rl.ac.uk/excitations.
[25] A. A. Ovchinnikov, Theor. Chim. Acta **47**, 297 (1978); D. J. Klein, C. J. Nelin, S. Alexander, and F. A. Matsen, J. Chem. Phys. **77**, 3101 (1982); O. Kahn, *Molecular Magnetism* (VCH, New York, 1993), and references therein.
[26] J. S. Miller and A. J. Epstein, Angew. Chem., Int. Ed. Engl. **33**, 385 (1994), and references therein.
[27] E. H. Lieb, Phys. Rev. Lett. **62**, 1201 (1989); **62**, 1927(E) (1989).
[28] J. A. Chan, B. Montanari and N. M. Harrison (to be published).