

## Magnetic Properties of C<sub>60</sub> Polymers

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(Received 23 May 2002; published 16 January 2003)*

Magnetic properties of various C<sub>60</sub> polymers are calculated using tight-binding molecular-dynamics and *ab initio* methods. Our results suggest a mechanism involving an interplay between structural defects and *sp*<sup>3</sup> hybridization to be responsible for the origin of this magnetism. The onset of magnetism is found to occur much more readily for the Rh-C<sub>60</sub> polymeric phase with defects than for any of the other polymers, in agreement with the recent experiment. Our estimate of the magnetic moment is also in very good agreement with the value observed in experiment.

DOI: 10.1103/PhysRevLett.90.026801

PACS numbers: 73.50.-h, 73.23.Hk, 73.61.Wp, 81.10.Aj

The discovery of C<sub>60</sub> cages with perfect icosahedral (*I<sub>h</sub>*) symmetry [1] has sparked tremendous interest in pure carbon compounds. This has led to extensive studies of fullerene based carbon solids [2]. The molecules in solid C<sub>60</sub> form a face centered cubic lattice (fcc) at room temperature with weak van der Waals type bonding between the molecules [2]. When exposed to visible or ultraviolet light, this molecular C<sub>60</sub> solid was observed to undergo a phase transformation resulting in a polymerized state in which the molecules are covalently bonded to each other [3]. Polymeric forms can also be obtained using high-pressure and high-temperature treatment of the van der Waals C<sub>60</sub> solid. Polymeric solids have been synthesized in one-, two- and three-dimensions.

Very recently, Makarova *et al.* [4] have reported the discovery of spontaneous magnetization in 2D polymeric C<sub>60</sub>. The magnetization is found to persist above room temperatures and up to 500 K. Magnetism in nonmetallic molecular materials is a welcome phenomenon from a technological perspective since these materials are usually less expensive to produce than their metallic counterparts. Furthermore, calculations suggest that a high attainable specific magnetization value (i.e., the magnetization/density ratio) may exist for these materials that may exceed that of  $\alpha$ -Fe [5]. Experiments have also confirmed the existence of magnetism in other carbon-based materials [e.g., activated carbon fibers (ACFs), fluorinated graphite, carbon foam [6–8]].

Makarova *et al.* [4] have attempted to investigate the magnetic properties of the C<sub>60</sub> polymer with a view to explain the origin of the observed magnetism. Their

measurements showed no evidence of ferromagnetic behavior in either their pristine fullerene powder or depolymerized samples, prompting them to rule out impurity effects as the possible cause of magnetism. The magnetic behavior is, therefore, attributed to the intrinsic properties of the C<sub>60</sub> polymer, such as ordered defect moments or itinerant ferromagnetism.

Despite the increasing experimental evidence for the existence of magnetism in various carbon-based materials, the precise mechanism for its origin is not well understood. The corresponding theoretical investigations [5,9–11] have been focused mainly on determining the most probable mechanisms that can lead to unpaired electrons and to their mutual interactions. Among the proposed mechanisms associated with the origin of magnetic carbon phases, two have been quite promising. The first is associated with the unpaired electrons that are provided by the edge carbon atoms (ECAs) of nanographitic particles. The other is attributed to the presence of carbon vacancies. In both mechanisms, one can underline the same basic ingredient. That is, the transformation of *sp*<sup>2</sup> to *sp*<sup>3</sup> orbitals in combination with some structural reconstruction. In particular, ECAs of nanographitic layers are found to contribute to carbon magnetism when the nanographitic layers in the particle are stacked in such a way that each graphene layer is relatively shifted with respect to the underlying one [9].

In polymeric carbon reported by Makarova *et al.*, magnetism has been found in the 2D rhombohedral C<sub>60</sub> (Rh-C<sub>60</sub>) phase but not in the 1D orthorhombic and the 2D tetragonal C<sub>60</sub> polymers; it has been attributed to

polymerization and most probably to deviations from the conventional polymerization process and the presence of defect patterns in the polymerized network [4]. The latter explanation was supported by the fact that strong magnetic properties were observed only in Rh-C<sub>60</sub> prepared at 1020–1050 K (that is, close to its stability limit). On the other hand, the presence of a carbon defect in the graphene lattice has been found to impose an in-plane relaxation and accommodate an extra charge giving rise to an unpaired spin [10].

In this Letter, we report results of our calculations of magnetic moments in low dimensional polymeric forms of C<sub>60</sub> in the presence of defects. Calculations are carried out using our tight-binding molecular-dynamics (TBMD) scheme incorporating the Hubbard approximation that allows dynamic simulations of magnetic properties in materials [12]. It has been shown that exchange-correlation effects beyond the conventional local density approximation (LDA) treatment might be important for the investigation of vacancies in carbon [13]. Studies incorporating electron correlations at the level of the Hubbard approximation have demonstrated the effectiveness of this approximation in the study of low-dimension carbon structures [14–17]. This is further supported by our recent TBMD studies on these systems [18]. Our TBMD method includes use of *s*, *p*, and *d* orbitals in order to provide the correct description of interatomic interactions in systems consisting of semiconductor and transition metal atoms as well as their heterosystems.

We consider 2D (rhombohedral and tetragonal) and 1D (orthorhombic) C<sub>60</sub> polymers containing a mixture of *sp*<sup>2</sup> and *sp*<sup>3</sup> bonded carbon atoms. We also consider an all *sp*<sup>2</sup> 1D C<sub>60</sub> polymer. All structures are fully optimized without any symmetry constraints using our TBMD scheme. The relaxed structures are shown in Fig. 1. The infinite polymers are simulated using supercells with periodic

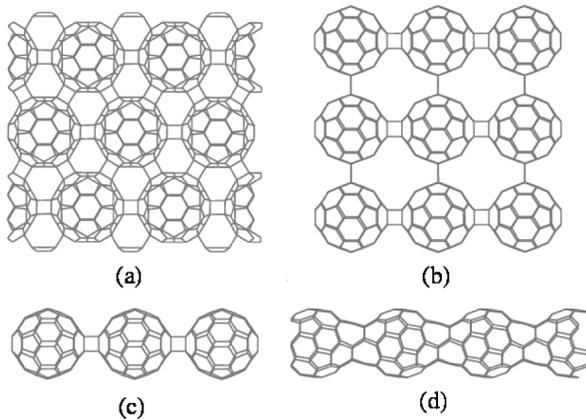


FIG. 1. Various 2D and 1D polymeric solids formed from C<sub>60</sub>. All structures are fully relaxed using the TBMD method. (a)–(c) contain mixed *sp*<sup>2</sup> and *sp*<sup>3</sup> bonded carbon atoms. Linear C<sub>60</sub> polymer with only *sp*<sup>2</sup> bonding is shown in (d).

boundary conditions. A constant pressure (“movable wall”) ensemble is incorporated into the supercell formalism that allows for a simultaneous relaxation of lattice and basis degrees of freedom [19]. A uniform grid consisting of 126 *k*-points were used in the calculation of forces. Magnetic moments are then calculated for all relaxed structures for different values of the magnetization (the intra-atomic exchange splitting) term, *s*<sub>0</sub>. We next investigate how the magnetic properties change in the presence of defects. We create vacancies by removing one carbon atom per C<sub>60</sub> unit in each of the structures in Fig. 1. Magnetic moments are calculated for the same set of *s*<sub>0</sub> values as used in the absence of defects after the structures are fully relaxed using the TBMD scheme.

Our results are summarized in Table I. From these it is observed that all structures exhibit magnetic ground states for values of the *s*<sub>0</sub> term exceeding a threshold value *s*<sub>0</sub><sup>th</sup> (lowest *s*<sub>0</sub> value). These results are in agreement with the findings of Bergomi *et al.* [16], who found that the C<sub>60</sub> fullerene and C<sub>12</sub> tetrahedron exhibit a magnetic instability for *U* = *U*<sub>th</sub>; for *U* ≥ *U*<sub>th</sub>, these systems exhibit a magnetic ground state which is like a generalized spin density wave (SDW) state. Our symbol *s*<sub>0</sub> is approximately related to Hubbard-*U* by the relation

$$s_0 = U\langle\mu\rangle/2, \quad (1)$$

where  $\langle\mu\rangle$  is the average magnetic moment per carbon atom. As Table I shows, the *s*<sub>0</sub> value depends sensitively on the structural details of the polymer. More importantly, structures with vacancies show substantial decrease in the *s*<sub>0</sub><sup>th</sup> when compared with their defect free counterparts. The lowest value of *s*<sub>0</sub><sup>th</sup> is attained for the Rh-C<sub>60</sub> structure with vacancies.

Using the spin concentration value obtained from electron spin resonance data Makarova *et al.* estimated the magnetic moment per electron to be 0.4  $\mu_B$ , where  $\mu_B$  is the Bohr magneton. Their sample had a mass of 3.2 mg. Using these data and the data given in their Fig. 3(a), the magnetic moment per C<sub>60</sub> unit for their sample is  $\approx 0.65$  bohr magnetons. Substituting this value along with the Hubbard-*U* value ( $\approx 10$  eV [14]) in Eq. (1) we obtain *s*<sub>0</sub> = 0.05 eV per atom for their sample. This is in very good agreement with our *s*<sub>0</sub><sup>th</sup> value (0.03 eV) for the Rh-C<sub>60</sub> in Table I.

TABLE I. Values of *s*<sub>0</sub><sup>th</sup> (in eV) for different structures considered in this work.

Structure	<i>s</i> <sub>0</sub> <sup>th</sup>	
	No vacancy	With vacancy
Rh-C <sub>60</sub> [Fig. 1(a)]	0.85	0.03
Tetragonal C <sub>60</sub> [Fig. 1(b)]	1.0	0.20
Linear A C <sub>60</sub> [Fig. 1(c)]	0.70	0.10
Linear B C <sub>60</sub> [Fig. 1(d)]	0.80	0.70

Our calculations, thus, give strong support to the role of vacancy in the generation of magnetic moment. While unpaired spins can result from vacancy formation, we must also consider other factors. The  $sp^2$ - $sp^3$  rehybridization resulting from the 2 + 2-cycloaddition mechanism at the interfaces may also give rise to unpaired spins. Because of the peculiarly high symmetry of the  $C_{60}$  molecule, both the Rh- $C_{60}$  and the tetragonal  $C_{60}$  polymers contain a mixture of  $sp^2$  and  $sp^3$  atoms. This is not the case in the 1D polymers, however. While Fig. 1(c) shows a linear  $C_{60}$  polymer with mixed  $sp^2$  and  $sp^3$  bonding (dominant structural unit in photopolymerized  $C_{60}$ , for which ferromagnetic properties have been reported [20]), another linear  $C_{60}$  polymer containing only  $sp^2$  bonding is shown in Fig. 1(d). It should be noted, however, that the structure in Fig. 1(d) is hypothetical and has never been observed, in contrast to the other three. As seen in Table I, the  $s_0^{\text{th}}$  value for the all  $sp^2$  linear structure (Fig. 1(d)) is much higher than that for the mixed case. This suggests an interplay between vacancy and  $sp^2$ - $sp^3$  hybridization rather than vacancy alone being responsible for magnetization.

We explore this interplay in more detail by performing an *ab initio* study of the electronic distribution in the Rh- $C_{60}$  polymer in the presence of vacancies and compare it with the defect free case. The Rh- $C_{60}$  polymer with defects is shown in Fig. 2. The atoms surrounding the vacancy are shown in red, while the  $sp^3$  atoms participating in the intermolecular linkage are shown in green. The *ab initio* calculations were performed using the GAUSSIAN 98 program [21].

In the defect free case there is an accumulation of excess negative charge ( $\approx 0.5e$ ) in the four atoms participating in intermolecular linkage between each pair of

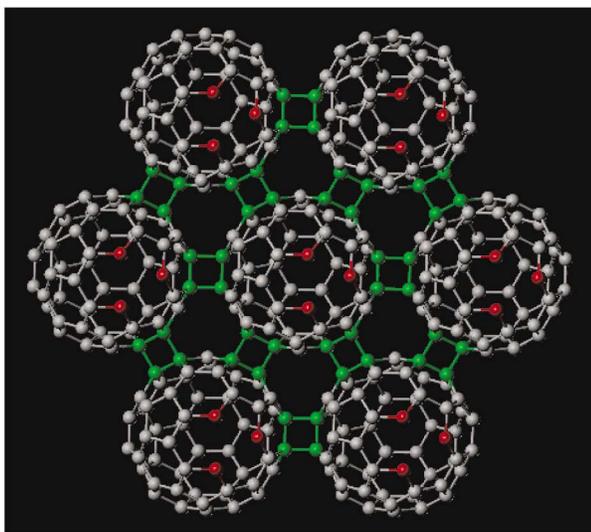


FIG. 2 (color). 2D rhombohedral  $C_{60}$  (Rh- $C_{60}$ ) polymer with one vacancy per  $C_{60}$  unit. The atoms surrounding the vacancy are shown in red, while the  $sp^3$  atoms are shown in green.

$C_{60}$  cages (all  $sp^3$ ). Furthermore, the occupancy of  $p_z$  orbitals is considerably higher than those of the  $p_x$  and  $p_y$  orbitals for these same atoms ( $z$  direction is taken to be perpendicular to the plane of the polymer). Neither the charge nor the  $p_z$  occupancy changes significantly after the creation of vacancy. The situation is considerably different, however, for the three atoms surrounding the vacancy in each  $C_{60}$  unit. They acquire excess positive charge ( $\approx 0.5e$ ) when compared with the defect free case. Creation of the vacancy leads to the appearance of excess spin density and nonzero spin magnetic moment associated with each  $C_{60}$  molecule. The accumulation of excess negative charge on the four-fold coordinated atoms forming the intermolecular link and an almost equal and opposite charge on the atoms surrounding the vacancy gives rise to an electric dipole moment. Our *ab initio* calculations give a dipole moment of magnitude 2.264 Debye per  $C_{60}$  unit for this system.

Our findings are in agreement with the generally accepted theory [22] according to which the origin of spins in carbon materials composed of  $sp^2$  and  $sp^3$  C-C bond network is attributed to the  $\sigma$  dangling bonds. The interfullerene (2 + 2)-cycloaddition processes can contribute to unpaired electrons by promoting them to higher orbitals enabling them to participate in the magnetic ordering. As pointed out by Makarova *et al.* [4], the interfullerene bonds are directed at angles different from the bond angle in diamond and are considerably less bound with dissociation energy only one-half of the diamond bond. The weakly bound electron can be readily available to participate in the magnetic ordering. However, in order for ferromagnetic coupling to occur there should be correlation between these spin moments. The spin moments here are sufficiently far apart and, therefore, the ferromagnetic coupling must be an indirect one requiring mediation. In the present case the dipole moment induced by the vacancy provides this mediation. The electrostatic interactions (i.e., Coulomb interactions between localized excess charges and between electric dipoles), thus, provide an effective exchange pathway for the intersite coupling of the spin magnetic moments. This mechanism may be considered analogous to the McConnell model [23] for intermolecular coupling.

The structural dependence of  $s_0^{\text{th}}$  is worth a look. It is reasonable to expect an inverse relationship between concentration of interfullerene bonds and  $s_0^{\text{th}}$ ; i.e., the larger the concentration of these bonds, the lower the  $s_0^{\text{th}}$  value. The  $s_0^{\text{th}}$  values for the tetragonal [Fig. 1(b)] and linear [Fig. 1(c)] polymers in Table I seem to contradict this assumption. It must be noted, however, that in the tetragonal case the planes formed by the pair of interfullerene bonds in the  $y$  direction is perpendicular to the planes formed in the  $x$  direction. The corresponding spin contributions are also directed perpendicular to each other in the two orientations.

Further insight can be gained by an investigation of the electronic band structure details of Rh-C<sub>60</sub> and tetragonal-C<sub>60</sub>. The highest occupied molecular orbital (HOMO) of Rh-C<sub>60</sub> is found to be doubly degenerate while that of tetragonal-C<sub>60</sub> does not appear to be degenerate [24]. These observations suggest that the proposed mechanism for the intermolecular coupling in the magnetic Rh-C<sub>60</sub> may be viewed in terms of a generalized flat band magnetism [25].

In summary, we have performed calculations of electronic and magnetic properties of various 2D and 1D polymers formed from C<sub>60</sub> cages using tight-binding molecular-dynamics and *ab initio* methods. Our results indicate that onset of magnetism is found to occur much more readily for the Rh-C<sub>60</sub> polymeric phase with defects than for any of the other polymers, in agreement with recent experiments. Our estimate of the magnetic moment is in very good agreement with the value observed in experiment. We have also offered a plausible mechanism for the origin of magnetism observed in experiment for these materials.

The present work is supported through grants by NSF (NER-0165121, ITR-0266277), DOE Grant No. 00-63857, NASA Grant No. 02-465679, EU-GROWTH research project AMMARE (Contract No. G5RD-CT-2001-00478), and the University of Kentucky Center for Computational Sciences. L.C. acknowledges support from RSTP grant (INTAS Grant No. 00-237) under the title "Topical Directions in Condensed Matter Physics."

*Note added.*—After the submission of our manuscript a new review article by Makarova (first author of the original paper reporting the finding of magnetism in C<sub>60</sub> polymers, Ref. [4]) has appeared [26]. The article reports TEM images showing that the samples are polymeric and crystalline in nature with negligibly small and undetectable amount of wracked fullerenes. Our model of periodically arranged defects in a stable crystalline structure, thus, satisfies the two conditions necessary for the fullerene network to become ferromagnetic: highly oriented structure and the presence of unpaired spins.

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