1 Introduction

1.1 Magnetic Carbon

Magnetism in organic materials is a welcome phenomenon from technological perspective since these materials are usually less expensive to produce than their ordinary metallic counterparts. Furthermore, they are light weight and known for low power consumption. Organic ferromagnets have theoretically a high attainable specific magnetization value (i.e., magnetization/density) that exceeds that of α-Fe. This property makes magnetic carbon potentially very useful. An organic magnet that responds to light could lead to new ways of storing and reading large amounts of computer data [1].

Ovchinnikov and Shamovsky [2] have predicted a ferromagnetic (FM) phase for pure carbon of mixed \( sp^2 \) and \( sp^3 \) bonded carbon atoms. The suggested FM state contains an equal number of \( sp^2 \) and \( sp^3 \) C-atoms per unit volume which corresponds to the maximum possible concentration (50%) of unpaired carriers (i.e., \( sp^2 \) C-atoms). The recent discovery of magnetic phase of the polymerized C\(_{60}\) materials [3–5], characterized by high Curie temperatures (500K [3], 820K [6]) and small saturation
magnetization values, has attracted the research interest from both theoretical and technolo
gical point of view.

However, this phenomena has also raised many basic questions regarding the possi
bility of the existence and the nature of magnetism in the C_{60}-based polymers
[7, 8]. These questions have their origin in the fact that these materials contain no
d or f electrons which are strongly interacting, while the new magnetic materials
develop a new type of magnetism based on weakly interacting s and p electrons.
Nevertheless, the experimental evidence keeps growing. Other graphite-based magnetic
materials have been discovered including, for example, the highly oriented pyrolytic
graphite (HOPG) [9], the graphite surface in the presence of carbon-adatoms [10], the
activated carbon fibers [11–13], graphite ribbons [14], the fluorinated graphite [15], the
hydrogenated nanographite, [16] the carbon foam [17], etc. At the same time, other
organic and inorganic magnetic materials have been discovered exhibiting common
features with the C_{60}-based FM polymers. Prominent among them are the TDAE-
C_{60} [18], the p-nitrophenyl-nitronyl-nitroxide (p-nnn) radicals [19–22], the hexaborites
[23–27], the oxides of rock-salt structure [28, 26], the cation-substituted oxides (i.e. Co
substituted cations in ZnO and TiO_2 [29, 30]), etc.

In the following we explore and identify the common features between the magnetic
carbon-based (specifically C_{60}-based polymers) and the other novel magnetic materials
referred to in the above. As will be shown, our exploration leads us to the pioneering
early works of McConnell [31, 32], Breslow [33, 34] and Ovchinnikov [2] on organic
ferromagnets. It will also be shown that electron-electron correlations in the presence of
structural defects appear to be the key factors for the development of the magnetic
phase in carbon-based materials and this justification can be extended to all the other
materials as well. In this view, the magnetic carbon-based and in particular the
C_{60}-based materials seem to belong to a sub-class of a new class of FM materials which
follow a common formation mechanism of ferromagnetism [35, 28]. This is classified
as defect-magnetism and, as it will be discussed in the following, it may be considered
as a generalized of the McConnell-II type magnetism.

1.2 Prerequisites for the Appearance of Carbon-magnetism

The explanation of the observed magnetism in the C_{60}-based polymers [3, 4] is a
two-fold issue [36]. First, an explanation of the existence of unpaired spins is needed.
This has to be followed by a theoretical justification of the origin of the long range
correlation that couples the unpaired spins into a FM alignment. The proposed
theoretical explanations are mostly focused at justifying the existence of unpaired
electrons and they all appear to converge on their origin which they attribute to the
structural and/or topological defects that either localize \pi electron states or contribute
to delocalized lone electron states associated with the defects [11, 15, 37–42]. As to the
origin of the FM coupling mechanism (FCM) which couples the unpaired electrons and
develops the FM state the answer is far from conclusive. In some reports the origin of
the FCM is either completely ignored or not satisfactorily justified.
[41, 40], while in others it is assumed that the FCM is originating from an exchange interaction similar to the $s-d$ interaction [11, 42, 37].

At present, we are far from a complete understanding of carbon magnetism. As referred to in the above, the development of the FCM appears to be the outcome of strong electron-electron correlations which, depending on the system, may manifest itself either as a charge and/or spin transfer process or as a flat band ferromagnetism or as a carrier-induced ferromagnetism or as a super-exchange process etc.

2 C$_{60}$-Polymers: A brief overview

For the sake of completeness, the basic properties of representative members of the C$_{60}$ polymers are briefly discussed in this section.

2.1 Preparation Methods of C$_{60}$-polymers

C$_{60}$-based polymers can be synthesized using:

- Photochemical methods [43], and
- high Pressure - High Temperature (HP-HT) methods [3–5, 44, 45].

Both types exhibit the same polymeric 2+2 cycloaddition bonds [46]. However, the photopolymers have a distorted fcc structure exhibiting a statistically random (isotropic) polymerization along all nearest neighbor (nn) directions (geometric frustration). On the other hand, HP-HT polymers display crystalline (ordered) structures. This results from the fact that an externally applied anisotropic stress selects the direction of polymeric bonding, which, in turn, relieves the frustration associated with the isotropic polymerization [47].

A pronounced characteristic of the newly discovered C$_{60}$-polymers is the experimentally found narrow windows, defined by pressure and temperature, within which magnetic C$_{60}$-based polymers can be found. These windows are approximately at the graphitization limit [48]. The C$_{60}$-based polymers are observed at the graphitization limit i.e., the limit at which the fullerene cages begin to break down, thus, justifying the assumption (see below) that the magnetic phase is associated with the appearance of structural defects in an otherwise (and experimentally verified) crystalline structure of these materials. It has also been verified that the magnetism of these samples is not influenced by the presence of the impurities they contain. The determination of any structural differences, however, between magnetic and non-magnetic samples by conventional characterization methods has not been possible yet [3–5].

2.2 Electronic Properties of C$_{60}$ Polymers

In the absence of vacancies we find all 2-D C$_{60}$-based polymers to be semiconducting with energy gaps in the range 0.3–1.0 eV, in agreement with reported band structure calculations [49–52]. As will be shown in Section 1, the presence of the vacancies induces states in the energy gap with the result that these materials become metallic or semi-metallic in the limit of infinite polymer with one vacancy per C$_{60}$ unit with the
exception of the liner C$_{60}$ polymer which exhibits $sp^3$ and $sp^2$ orbitals [36] and shows a very narrow gap.

3 Carbon Magnetism: A Member of a New Magnetic Class?

Based on a series of theoretical calculations, we have recently proposed a model for explaining the magnetic phase of the polymerized-C$_{60}$ materials [36]. The basic assumption of our model is the existence of vacancies in an otherwise pristine crystalline structure as intimated by the experimental results of Makarova and collaborators [3-5]. We demonstrated that the existence of the [2 + 2] cycloaddition bonds (which provide $sp^3$-bonded carbon atoms) in coexistence with vacancies can explain the origin of the magnetism in the polymerized-C$_{60}$ materials. In particular, we have shown that the vacancies and the [2 + 2] cycloaddition bonds provide, on the one hand, the unpaired electrons while on the other hand ignite charge transfer processes which create and sustain large electric dipole moments. The latter develop the FCM among the unpaired spins and lead to the development of a FM state. In such a mechanism, the electron-electron correlations play a crucial role as they promote the high spin-multiplicity states and make them energetically more favorable.

Concurrently with our model, another vacancy-based model has also been reported in an effort to explain the magnetic phase of oxides of rock-salt structure (i.e., CaO) [28]. A comparison between these two works provides the necessary motivation to explore to see if the defect mechanism can be used in justifying the appearance of magnetism in the materials referred to in Sec. 1. A careful study of both classes of materials i.e., the carbon-based and the non-carbon based ones, referred to in the above seems to reveal some common underlying features relevant to the nature of the associated magnetism in these materials. These are summarized in the following subsection.

3.1 Common Features of Carbon- and other Organic and Non-traditional Inorganic Ferromagnets

The most pronounced common features in the carbon-based and other organic or non-traditional inorganic magnetic materials are found to be the following [35]:

- The presence of defects (structural and topological) in an otherwise crystalline structure.
- The development of significant charge and spin transfer.
- The existence of a degenerate ground state driven by electron-electron correlations, and (in some cases) the presence of a resonant ground state.

3.2 Additional Features Exhibited by C$_{60}$-based Polymers

The magnetic C$_{60}$-based polymers exhibit some additional features that are worth noting. In particular, it was pointed out that the FM samples of C$_{60}$-based polymers have always been found to be in a crossover regime for a metal-insulator (M-I) transition [5]. Furthermore, band structure calculations revealed that some C$_{60}$-based polymers exhibit
flat or partially flat bands around the Fermi energy, $E_F$, and naturally the questions arise: Is the magnetism of the C$_{60}$-based polymers related to a M-I instability [5]? Is it a demonstration of flat-band ferromagnetism [53, 54]? Is it the result of structural frustration [47]? The resolution of these questions form the basis of the current investigations and are discussed in the following.

4 Defects in Carbon-based Materials

The emerging field of carbon nanoscience seems to draw much of its useful information from the basic graphite system. As Makarova et al., observed [5], the magnetism in the C$_{60}$-polymers cannot be seen independently of the graphitic magnetism. Therefore, a first step in examining the role of C$_{60}$-point defects in the polymerized C$_{60}$-magnetism is the study of the corresponding graphite counterpart, i.e., point defects in graphite and the role they play in the graphite magnetism.

It is also quite instructive to recall the basic properties of (carbon) conjugated polymers due to their similarity with the polymerized C$_{60}$. It should be noted that the conjugated polymers are semiconductors with a single band-gap of 1–3 eV but with the same mechanical properties as those of plastics. A prototype conjugate polymer which is of interest to our study is the polyacetylene (CH)$_n$,; it contains a backbone of $sp^2$-bonded C-atoms with the energetically highest valence electron occupying a $p$-orbital perpendicular to the plane of the nuclei; these $\pi$-orbitals appear close to the Fermi energy and a pairing mechanism among them leads to alternating single (longer) and double (shorter) bonds. However, it is worth noting that the distribution of the $\pi$-electrons may be drastically changed in the presence of perturbations, mainly those imposed by defects [55].

As stated above, defects seem to play a dominant role in the development of the carbon magnetic phase. In the present work, the term “defect” is ascribed to any type of point and/or structural and/or topological defects including vacancies [56], edge states [38, 39], substitutional impurities [29], Stone-Wales defects in graphite-based materials [40], orientational changes (as for example, among the C$_{60}$ molecules in the TDAE-C$_{60}$) [18], adsorbed adatoms [10], etc. Most of these defects play more or less the same role in promoting a FM ground state. That is, they break the sequence of the alternating single-double carbon bonds inducing the response of the material in the form of charge and spin transfer that leads to the formation of lone electrons and the possibility for a stable FM ground state. Thus, magnetic carbon phases have been reported for proton-irradiated HOPG [57], functionalized graphite particles [15, 16], graphite with carbon adatoms [10], etc. In all these cases, the defects break the local symmetry and the system responses for healing it. Before entering into the details of their role in FM carbon-based materials, we discuss two such defects which are related to the ferromagnetism in the C$_{60}$-based polymers, i.e., the vacancies and the 2+2 cycloaddition bonds. Other type of defects will be discussed in section 5.
4.1 Vacancies

The vacancies are created by removing one or more carbon atoms; they lead to under-coordinated C-atoms. The experimental results on graphite vacancies have mainly been obtained from STM and TEM studies. It has been widely accepted that the symmetric (D_{3h}) vacancy is the most common mono-vacancy in graphite. However, recent reports claim that the asymmetric vacancy 5-1db (pentagon-one dangling bond) with (experimental) formation energy of 7.0 ± 0.5 eV has lower energy while the symmetric vacancy is a result of a time-averaged superposition of three degenerate vacancy-states alternating by a thermally activated Jahn-Teller effect [58]. (This result has been questioned recently by Ma et al. [59] who attributed the results of Barbary and collaborators [58] to artifacts and/or limitations of the computational approach used in reference [58]). It has also been found that the ground state vacancy in graphite is spin-free.

Contrary to what was initially anticipated, Hjort and Stafstrom using the Hückel approximation found that the triad of carbon atoms near a graphite vacancy do not contribute to the system with three \( \sigma \)-type \( sp^2 \) dangling orbitals but with four \( \pi \)-type \( sp^2 \) electrons [56]. The relaxation of this triad of atoms is found to be entirely in plane with the carbon atoms next to the vacancy site relaxing by moving away from the vacancy site. Furthermore, it was found that each of these carbon atoms gets approximately 0.19 electrons originating from states near the Fermi energy. The latter finding were claimed to be justified by STM measurements in which the vacancy is viewed as a bright spot (protrusion).

The results of Ref. [56] were recently called into question by Andriotis et al., who argued that the vacancy sites create a charge-density-wave-like (CDW-like) disturbance, with positive charge accumulation of approximately 0.5 electrons and an electric dipole moment (EDM) of 0.39 Debyes [60]. The same picture was found to develop also around a vacancy in the C_{60}-based polymers, but in this case the calculated EDM was found to be much larger (2.264 Debyes) [36]. Furthermore, it was found that carbon atoms surrounding the vacancy in graphite exhibit lone electrons and, thus, the vacancy appears to be the provider of unpaired spins.

4.2 The [2+2] Cycloaddition Bonds

The [2+2] cycloaddition bonds that are formed during the polymerization process can be considered as a different type of defect that breaks the alternating single and double bonds in the C_{60}-polymers. The formation of these bonds requires that neighboring C_{60} molecules be oriented with their double bonds parallel to each other [46, 61]. A complete polymerization leads to an average inter-C_{60} distance of 9.1–9.2 \AA

(= 1 Å, by comparison, at ambient pressure). This bond is also known as a 66/66 bond because it involves two pairs of bonds that are shared by two hexagons in a C_{60} molecule. It may also happen that one or both bonds that are linked by the cycloaddition be shared between a hexagon and a pentagon. The resulting cycloaddition bonding then may be of the type 65/66 or 65/56, respectively. The relaxed
66/66, 65/56 and 65/66 bonds were found to have length 9.19, 9.17 and 9.26 Å, respectively [45].

5 Theoretical Models

We have classified the various theories proposed for the origin of magnetism in the organic and other non-traditional inorganic materials in three general categories according to their basic and characteristic feature of the proposed mechanism for magnetism. These are: (i) the defect-related theories, (ii) the charge and spin transfer theories, and (iii) the band magnetism theories one of which is the carrier induced ferromagnetism discussed below.

5.1 Defect-related Theories

The role of the defects appear to be multiple. Firstly, they provide unpaired electrons and help in their delocalization. Secondly, they break locally the symmetry of the crystalline structure. This has, as a consequence, the development of intra-molecular charge and spin density transfers which change the relative stability of the high spin states which may become energetically the most favorable configurations for the ground state. In some cases this process is facilitated by the existence of a resonant ground state (as for example in the case of the TDAE- C$_{60}$ [18] and the p-nm radicals [20–22, 19]. It is worth mentioning that in carbon-based materials the defects are developing conditions found in the various levels of the proposed McConnell model [31–34] and create the starred and un-starred C-atoms (non Kekulé structures) extensively discussed within the Ovchinnikov’s spin-polarization model [2]. Thus, it is observed that defects introduce a perturbation that alters the features of the bonding among the carbon atoms as in the case of the perturbed conjugated polymers.

5.1.1 Other Structural and/or Topological Defect-related Theories

The vacancies and the other structural defects discussed in Sec. 4 have one common characteristic: They can provide unpaired electrons which, in turn, provide the spin-magnetic moments.

Besides vacancies another very common defect is the one known as the Stone-Wales defect [62]. This is formed in a graphene lattice by a C-C bond rotation of 90° transforming, thus, a four-adjacent hexagon-structure into one consisting of two heptagons and two pentagon adjacent to each other. Kim et al. [40] claimed that a partly opened intermediate structures obtained by transforming a C$_{60}$ molecule into a nanotube by a series of Stone-Wales defects are magnetic. This mechanism was proposed as a possible explanation for the observed magnetism in C$_{60}$-based polymers.

According to Park et al. [41], defects appearing in all-carbon nanostructures exhibiting negative Gaussian curvature are associated with sterically protected carbon radicals which result in the presence of heptagons in an an otherwise hexagon-based structure. These carbon radicals acting in groups of three provide a delocalized lone
electron, providing free electron spins. However, in this report as well as in Ref. [40] the FCM mechanism which is necessary for the FM state to be built up has not been addressed convincingly.

Finally, in nano-graphitic particles defects which result by translating one graphite layer with respect to its neighboring ones (stacking defects) were found to exhibit magnetic ground state [38, 39]. In these nano-graphitic systems, the exotic magnetism is related with the \( \pi \)-states localized mainly at carbon atoms on the zig-zag edges of each nano-graphitic layer. A similar picture is seen in nano-graphene ribbons with zig-zag edges. These systems are characterized by partially flat bands which cause a sharp peak in the electron DOS at the Fermi energy. Furthermore, the zig-zag graphene ribbons exhibit a charge-polarized state which is stabilized in the presence of nearest neighbor Coulomb interactions and becomes competitive in stability with the spin-polarized state in an external electric field [63].

5.1.2 Frustrated Systems

Polymerization of \( \text{C}_{60} \) leads to polymeric \([2+2]\) cycloaddition bonds resulting in the development of significant lattice strains the latter being proportional to the number of the polymerization bonds developed. Polymeric \( \text{C}_{60} \) systems belong to the class of the frustrated systems. Their basic characteristic is that they exhibit a large number of isoelectronic configurations and, consequently, have a distorted ground state with macroscopic degeneracy [47]. The vast degeneracy of their classical ground state makes them highly susceptible even to small perturbations. Such a system can be viewed as being in a Resonant Valence Bond (RVB) state which is defined as a coherent superposition of the various possible arrangements of all the valence bonds of the system with no crystalline long-range order. The RVB state is stabilized by lattice deformations (phonons) which increase the hopping energy across the valence bonds. A very interesting property of the frustrated systems relevant to the present study is the observation that in some frustrated systems magnetic ordering can occur in the presence of external fields. This is because a large degree of the geometric frustration can be healed through a coupling between spin and lattice degrees of freedom. A particular example is the system \( \text{Ho}_3\text{Ti}_2\text{O}_{12} \), which does not exhibit long magnetic order (up to at least 0.35K) in zero magnetic field. However, upon applying a field, ordered phases are observed. More importantly, the presence of defects (i.e., dangling bonds in a RVB system) switch on the resonating process among the various valence bond configurations which can lead to a more stable ground state. It is quite interesting to note that such defects can extend over several sites and be quite mobile (case of polyacetylene).

5.2 Charge and Spin Transfer Theories

The McConnell-II model [32], extended by Breslow [33, 34], predicts that a quasi-1D ionic material \( D^+A^- \) built up from positive ions of the donor molecules \( D \) and the negative ions of the acceptor \( A \) can exhibit a FM ground state if either the donor or the
acceptor molecule have a triplet neutral ground state. In such a case back charge transfer mixes the neutral triplet ground state with the triplet charge transferred state of the ionic state leading to a FM coupling.

The McConnell-I model [31] predicts that a FM spin-coupling may result in systems which exhibit large positive and negative atomic π-spin densities suitably packed so that atoms of positive spin density are exchange coupled to the atoms of negative spin density in neighboring molecules. This becomes evident by rewriting the Heisenberg Hamiltonian

$$H^{4b} = -\sum_{\langle ij \rangle} J_{ij}^{4b} S_i^z S_j^z$$

as

$$H^{4b} = -S_i^z S_j^z \sum_{\langle ij \rangle} J_{ij}^{4b} \rho_i^\pi \rho_j^\pi,$$

where $J_{ij}$ are the exchange integrals, $S_i^z$ and $S_j^z$ denote the π-electron spin on atom $k$ of molecule $X$ (the total spin of molecule $X$) respectively and $\rho_k^\pi$ is the spin density on atom $k$ of molecule $X$.

For such materials, the theoretical studies are focused at the determination of the effective exchange interaction $J_{ij}$ and determine the orbital-orbital (OO), $J_{ij}^{oo}$ and the spin density product (SDP) contribution $J_{ij}^{sdp}$ [64, 65].

5.3 Carrier-induced Ferromagnetism

The carrier-induced ferromagnetism is another concept that has been introduced in explaining the observed ferromagnetism in dilute semiconductors. According to this approach, the carriers (electrons or holes) become nearly bound to the magnetic impurity sites by getting strongly coupled to the localized magnetic moments. The carriers experience a spin dependent interaction with the magnetic impurity (translated as a spin dependent energy of the impurity-site). The impurity band becomes broader for the FM than the PM state with the result the FM state to become energetically more favorable. The hopping of carriers among the impurity sites causes the FM ordering of the localized spins through the double-exchange mechanism. (See for example, Ref. [66] where this concept is applied using the dynamical coherent potential approximation (CPA)).

6 Magnetic C₆₀ Polymers Revisited

The magnetic C₆₀-based polymers prepared with the HP-HT method are frustrated systems (see Sec. 2) and, therefore, one could assign their magnetism to the consequences of the frustration. On the other hand, their preparation conditions do not exclude the presence of point defects (i.e., vacancies, Stone-Wales defects,
2+2 cycloaddition bonds of various character - bond orientational defects - , etc). Thus, polymerization, frustration and point defects acting independently or in a synergetic way lead to structural and/or topological instabilities to which the system reacts with charge transfers and/or by coupling charge, spin and lattice degrees of freedom. Such processes being assisted by electron-electron (e-e) correlations allow states of high-spin multiplicity to appear as the energetically more favorable one for the ground state.

In the following, results for the C_{60} based polymers obtained by performing tight-binding molecular dynamics (TBMD) simulations as well as the ab initio methods are discussed.

6.1 Tight-binding Molecular Dynamics Simulations

In theoretical treatments in which defects and e-e correlations are omitted, no magnetic ground state is found for the C_{60} based polymeric materials. It has been shown that calculations carried out using the tight binding (TB) approximation incorporating the Hubbard-U approximation to the e-e correlations can be used successfully to describe carbon-based magnetic materials [39, 67-72]. This is further supported by our recent studies on these systems using our TBMD scheme at the Hubbard-U level of approximation to the e-e correlations (to be denoted as the U-TBMD method). Our U-TBMD method includes use of s, p and d orbitals in order to provide the correct description of inter-atomic interactions in systems consisting of semiconductor and transition metal atoms as well as their hetero-systems. The method has been successfully used to study not only the carbon-based materials [73], but also the magnetic clusters consisting of transition metal atoms (TMAs) [72, 74, 69] as well as their interaction with low-dimension carbon surfaces (graphite, C_{60}, single-wall carbon nanotubes (SWCNs), benzene molecules, etc) [75-77].

Fig. 1. 2-D rhombohedral C_{60} (Rh- C_{60}) polymer with one vacancy per C_{60} unit. The atoms surrounding the vacancy are shown in green, while the sp^3 atoms participating in the [2+2] cycloaddition are shown in magenta.
Fig. 2. Band structure for the Rh-\(C_{60}\) polymer with one vacancy per \(C_{60}\) unit (left), density of states (DOS) (middle) and DOS in the absence of any vacancy (right). The Fermi levels are indicated by dashed lines.

In our studies we considered 2-D (rhombohedral and tetragonal) and 1-D (orthorhombic) \(C_{60}\) polymers containing a mixture of \(sp^2\) and \(sp^3\) bonded carbon atoms. We also consider an all \(sp^2\) 1-D \(C_{60}\) polymer [36]. The infinite polymers were simulated using supercells with periodic boundary conditions. We created vacancies by removing one carbon atom per \(C_{60}\) unit in each of the structures. All structures were fully optimized without any symmetry constraints using our TBMD scheme. The relaxed polymer in the 2D rhombohedral-\(C_{60}\) (Rh-\(C_{60}\)) structure with one vacancy per \(C_{60}\) molecule is shown in Fig. 1. In Fig. 2 we present results for the band structure for this polymer (left panel), while the electron density of states (DOS) is shown in the middle panel. For comparison, we present the vacancy-free DOS in the right panel.

As is clear from Fig. 2, the introduction of vacancies induces a dramatic change in the Rh-\(C_{60}\) polymer; they change it from a semiconductor into a semi-metal. This is in accordance with the experimental results which find that the magnetic phase of the Rh-\(C_{60}\) polymer is found at a crossover regime for a metal-insulator transition [5].

6.2 \textit{Ab initio} Calculations

In order to get and in depth understanding of the origin of the changes that take place in the \(C_{60}\)-based materials upon polymerization and the development of their magnetic phase, we performed \textit{ab initio} calculations in a \(C_{60}\)-dimer with and without vacancies. In the latter case we assumed one vacancy per \(C_{60}\) molecule as with our TBMD simulations. All \textit{ab initio} calculations were performed with the GAUSSIAN 03 program package using density functional theory (DFT) with the three-parameter hybrid functional of Becke combined with either the Lee-Yang-Parr correlation functional or the Perdew-Wang 1991 gradient-corrected correlation functional [78]. The atomic basis set that was used is of double zeta quality and includes relativistic effects for heavy atoms.
Our initial computational results verified that the defect-free dimer has a singlet ground state. For the dimer with the vacancies it was found that the ground state is a triplet which is found to be 1.905 and 0.816 eV lower that the singlet and quintet states, respectively [79]. These results are in agreement with both theory and experiment [3, 36] according to which a magnetic moment of approximately one Bohr magneton (1 $\mu_B$) per C$_{60}$ molecule is expected for the C$_{60}$-based polymers.

In Fig. 3, we show the charge transfer that is induced by the vacancies in a C$_{60}$-dimer. In this graph, two striking features are immediately noticed. The first is that there is a depletion of electrons from each vacancy region (which appear positively charged) and at the same time there is an accumulation of charge in the [2+2] cycloaddition bonds. The second feature is that a charge density wave-like (CDW-like) disturbance develops around each vacancy which does not die away. Instead, being assisted by the opposite charge accumulation around the [2+2] cycloaddition bonds, it joins up smoothly with the CDW-like disturbance around the neighboring vacancy. The developed electric dipole moment (EDM) is rather large (2.264 Debyes per C$_{60}$ molecule). It is worth noting that a similar ab initio study of the vacancy in a graphene sheet gave us the same picture for the charge transfer around the vacancy as in the C$_{60}$ dimer case. However, in the case of the graphene sheet with a vacancy, the calculated EDM is found to be much smaller (0.39 Debyes). This is a noticeable difference between our results and those of Ref. [56]. Another difference is that in our case the carbon atoms around the vacancy move towards the vacant site upon relaxation while in the case of Ref. [56] they move away.

Contrary to the charge delocalization, the spin density appears localized around the vacancy cites.

![Image of the effect of charge transfer induced by the vacancy and the presence of [2+2] cycloaddition. The atoms surrounding the vacancy are positively charged while the atoms participating in the cycloaddition are negatively charged.](image)
7 Discussion and Conclusions

A careful comparison of our results with those reported for various other non-related systems, but exhibiting $s-p$ magnetism, allows us to observe many basic common features discussed earlier (see section 1). Subsequently, it has been realized that these systems develop significant charge transfers and a case can be made for these systems to be considered as generalized McConnell ferromagnets. In this section we take this observation further and complete the present investigation with our conclusions.

7.1 Generalized McConnell Ferromagnetism

It must be emphasized that the $s-p$ magnetism observed in carbon based materials as well as in other organic and non-traditional inorganic materials is a consequence of strong e-e correlation effects. The latter lead to ground states that can be described as a superposition of states of various spin multiplicities and manifest themselves as FM-configurations when the high-spin-spin multiplicity states are dominant. In the ferromagnetic charge transfer salts, described by the McConnell model [31–34], such a possibility arises when either the acceptor or donor molecules exhibit triplet ground state (see Sec. 2). In these systems, the acceptor and donor sites are assigned to molecules of different kinds. On the other hand, in the case of the defect magnetism, which appears to be the case for the $C_{60}$-based polymers and other organic and non-traditional inorganic magnetic materials, one kind of defects (i.e., vacancies) play the role of the donor molecules while coexisting defects of another type (i.e., 2+2 cycloaddition bonds) play the role of the acceptor molecules. The ferromagnetism, in this case, depends on the ability of the defects to create and sustain electric fields which bind the charge in the atoms around the defects and provide the necessary kinetic exchange for promoting the high spin states as the energetically more favorable ground state. In this view, the defect magnetism of the $C_{60}$-based polymers and that of other organic and non-traditional inorganic magnetic materials can be considered as a generalization of the McConnell model [31–34].

Looking at it from a different angle, the donor and/or the acceptor sites can be considered as the main sources which induce lone pair electron orbitals and provide unpaired spins; the emphasis here is focused on the ability of the defects to develop the necessary interaction pathways among the unpaired spins and establish the necessary FCM.

In both views, the role of the charge transfer is crucial; it can be achieved by the development of sufficient charge delocalization. The delocalization may be global [41] or it may extend over a small number of either trivalent or tetravalent C-atoms [60]. The latter type of delocalization is analogous to that appearing in alternant hydrocarbons in which the unpaired electrons are distributed over only the active carbon atoms [80]). According to our calculations, the majority of the delocalized molecular orbitals of the $C_{60}$-polymers, the delocalization is of the form of a through-space homoconjugation [81] or hyperconjugation [82]. This delocalization leads to an overlap between an electron in its $2p_z$ orbital with an $sp^2$ orbital in an adjacent or remote C-C bond.
The development of the delocalization can be related with the findings that some defect-based magnetic materials are either metallic or semi-metallic. This is supported in the case of the Rh-$C_{60}$ polymer where the band structure of the relaxed system with one vacancy per $C_{60}$ unit shows the system to be semi-metallic (see Sec. 1).

The conditions under which organic materials appear as generalized McConnell ferromagnets depend strongly on two factors. The first being the existence of generalized donor and acceptor sites in the material and second being the OO and SDP contributions to the effective exchange interaction $[64, 65]$ among the donor and acceptor sites (see Sec. 2). Thus, factors like geometry and symmetry, frustration, delocalization of molecular orbitals and energy spectrum of the lowest excited states $[83]$ are expected to be among those which determine the appearance or not of a generalized McConnell ferromagnet.

In the ferromagnetic $C_{60}$-based polymers, the optimum conditions for the creation of donor and acceptor sites seem to be achieved in the presence of structural and/or topological defects in an otherwise crystalline structure of these materials. In these, the role of the defects appears to be in the development of strong EDMs locally which promote the contribution of the high-spin-multiplicity states to the ground state and sustain the required conditions for establishing the FM ground state. This role of the defects was sufficiently demonstrated by our ab initio calculations.

7.2 Other Possible Generalized McConnell Ferromagnets

A donor-acceptor type magnetic material that can be characterized as a generalized McConnell-II ferromagnet is the TDAE-$C_{60}$ in which the defects originate as a consequence of changes in the mutual orientation of adjoining $C_{60}$ units $[18, 84]$. However, a characteristic example of non-carbon based magnetic material of the proposed generalized McConnell type appears to be the case of the defect-magnetism of CaO in which a recent study $[28]$ has demonstrated that Ca-vacancies lead to a FM state while oxygen vacancies do not. In another example, namely the case of ZnO where Zn atoms are substituted by Co or Mn $[85]$, it was found that the FM-state is stabilized if concurrently with the substitution of Zn by Co the system exhibits Zn vacancies or it is doped by Cu$^+$ ions. It is worth noting that the ZnO system which is simultaneously doped by Co and Cu is in complete analogy with the ferromagnetic $C_{60}$ polymers. That is, both systems exhibit two kinds of defects which act as donor and acceptor atoms; they are just members of the same class of magnetic materials that can be characterized as ferromagnets of the generalized McConnell-II model. Other possible members of this class may be the hexaborites (i.e., $CaB_{6}$ with $B_{6}$-vaccancies) $[23, 26]$, the TiO$_2$ in which Ti is partially replaced by Co $[29]$, conjugated polymers (with number of starred C-atoms different than that of the unstarred ones $[80, 2]$), etc.

7.3 Band Ferromagnetism

Looking from the band structure point of view, our results indicate an additional role of the defects. That is, their association with the narrowing of the energy gap at the Fermi level which has as a result the semiconducting defect-free $C_{60}$-polymers to
become semi-metallic in the presence of defects. This has as a consequence the 
delocalization of the of lone electron orbitals which may then act as mediators for 
establishing the coupling among the unpaired spin-moments. In this sense one can 
attribute the magnetic state of these materials in the mediated coupling of the 
delocalized orbitals in a way analogous to the $s-d$ type of interaction in transition 
metals. In our opinion, this is not exactly the case. The mediated coupling in the $s-p$
materials provides rather the means for a kinetic exchange stabilization of the magnetic
state relative to the non-magnetic one. However, it has to be pointed out that both terms
used i.e., the $s-d$ coupling and the kinetic exchange denote expressions related to
the description of the level and the way the $e-e$ correlations are treated in each of the above
described methods and therefore they can be understood as complementary descriptions
of the same underlying physics.

For analogical reasons we can exclude the justification of the carrier induced
ferromagnetism (see Sec. 3).

Finally it should be noted that our results also do not support the case for flat band
ferromagnetism in the C$_{60}$-based polymers [53, 54]. In fact, 2D-rhombohedral and the
1D C$_{60}$-polymers do exhibit either partial or complete flat bands when vacancy-doped.
This may be associated with a degenerate ground state. However, it is difficult to check
whether the local connectivity condition is satisfied [53, 86], especially in the case of
the Rh- C$_{60}$ polymer. It may be only the magnetism of the 1D-polymers with vacancies
to be amenable to the class of the flat band ferromagnetism as this material shows flat
bands at $E_F$ and it is probable that can satisfy the local connectivity condition.

7.4 Conclusion

The magnetism of the C$_{60}$-based polymers maybe justified as a generalized
McConnell magnetism. This is a consequence of a kinetic exchange stabilization of the
magnetic state rather than a carrier induced or flat-band ferromagnetism. The
generalized McConnell ferromagnetism is facilitated by the presence of structural and
topological defects which develop the necessary charge transfers and, associated with
them, exchange interaction pathways.

The above observations may be helpful in designing new magnetic materials of the
generalized McConnell-II type. The recipe is simple. That is, to check whether doping
can provide to the system charge centers of both sign (negative and positive) which are
associated with unpaired spins and at some particular concentration these defects can
provide the necessary FCM among the free spins.

In view of this recipe, it does not appear necessary to look only for donors or
acceptors with triplet ground state. Instead, one can also search for materials with those
kind of defects which can give rise to charge transfer with associated electric fields
strong enough to promote a high-spin state as the most favorable ground state.
Acknowledgments

The present work is supported through grant by EU-GROWTH research project AMMARE (G5RD-CT-2001-00478), NSF (ITR-0221916), DOE (00-63857), NASA (00-463937), and the Kentucky Science & Technology Corporation (03-60214).

References

13. The activated carbon fibers are a kind of microporous carbon material consisting of a 3-D network of 2–3 nm micrographites whose edges are covered with functional groups and dangling bonds. Each micrographite is formed with a stack of 3-4 nanosized graphene sheets. 12
48. The graphitization process is the heat treatment of carbonaceous material at high temperature in contradistinction to the carbization process which refers to the low-temperature treatment 12.
79. All calculations were performed on the relaxed geometry of the triplet state.