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## Defect-originated magnetism in carbon-based and non-traditional inorganic compounds: A new class of magnetic materials

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**Abstract.** – Magnetism in organic and non-traditional inorganic materials (NTIMs) is a fascinating phenomenon from both scientific and technological perspective. Recent experimental discovery of ferromagnetism in organic C<sub>60</sub>-based polymers has challenged the traditional concepts of the origin of magnetism. Although the nature of the *s-p* magnetism of the C<sub>60</sub>-based polymers has been distinguished from the nature of the newly observed magnetism in NTIMs, a defect-based picture of magnetism is found to provide a common thread connecting all these materials. As shown in the present work, this magnetism can be considered as a generalized form of the well-known McConnell model, thereby providing a unified classification of these magnetic materials and elucidating its common origin with the *d-ferromagnetism*.

The recent discovery of spontaneous magnetization in 2D polymeric C<sub>60</sub> at room temperature by Makarova *et al.* [1,2] provided a theoretical challenge since this *exotic s-p* magnetism appeared to be different in nature from that of the traditional *d-ferromagnets* (*e.g.*, Fe, Co, Ni). All the theoretical works aimed at explaining the mechanism responsible for this magnetism are almost exclusively focused on justifying only the existence of unpaired electrons; there seems to be a consensus as to their origin which is attributed to the structural and/or topological defects which either localize  $\pi$  electron states or contribute to delocalized lone electron states associated with the defects [3–8]. 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 [3–5, 8, 9].

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Magnetic phenomenon in *s-p* systems is an exciting new prospect both from fundamental scientific and technological viewpoints. A microscopic understanding of the origin of this magnetism in organic and non-traditional inorganic materials (NTIMs) can be a very useful tool that can effectively be used in their controlled production, leading to a new generation of fast and inexpensive devices.

In this letter, we present a mechanism for the microscopic origin of the observed ferromagnetism in polymerized fullerenes and show that the same underlying mechanism can be invoked in the case of NTIMs. Our conjecture is based on the analysis of defect-related magnetism reports in carbon-based as well as in NTIMs that reveal the existence of several common features including [10]: i) The presence of defects in an otherwise crystalline structure, ii) the development of significant charge and spin transfer, iii) the existence of a degenerate ground state and, in some cases, iv) the presence of a resonant ground state. Based on these observations, we present here a mechanism for the microscopic origin of the observed ferromagnetism in polymerized fullerenes and show it to belong to a general class of phenomena describable using a generalization of the McConnell model [11,12]. We also demonstrate that this generalization can be used to unify the magnetic behavior of many newly synthesized ferromagnets and elucidate its common origin with the *d-ferromagnetism*. The results presented in this work are obtained using both *ab initio* and tight-binding molecular-dynamic (TBMD) methods. All structures are fully relaxed with no symmetry constraints [13]. All *ab initio* molecular orbital calculations were carried out with the Gaussian 03 program package using the UB3LYP density functional theory (DFT) method with the 6-311G\*\* basis set [14].

We consider the 2D rhombohedral C<sub>60</sub> (Rh-C<sub>60</sub>) polymeric phase with and without the presence of defects. In our TBMD calculations we use a supercell to simulate the infinite 2D polymer with two C<sub>60</sub> units as basis. We repeat our calculations for the same system with one defect per C<sub>60</sub> unit (see fig. 2 in ref. [15]). Both structures are found to be stable on relaxation. Correspondingly, in our *ab initio* calculations, we use a C<sub>60</sub> dimer with and without one vacancy per C<sub>60</sub> unit. Both structures are stable on relaxation with the *ab initio* method as well.

The TBMD results show that the defect-free Rh-C<sub>60</sub>-polymer is a semiconductor and the magnetic state is not the energetically most favorable ground-state configuration. In the presence of vacancies, however, the Rh-C<sub>60</sub>-polymer becomes a semi-metal (see fig. 1) and its magnetic state (exhibiting magnetic moment of 1  $\mu_B$  per C<sub>60</sub> molecule) becomes an energetically favorable configuration for the ground state [15]<sup>(1)</sup>. Furthermore, the magnetization value of the Rh-C<sub>60</sub>-polymer is found to be considerably higher than those for tetragonal or linear C<sub>60</sub> polymers with vacancies. All these are in very good agreement with the experimental results of Makarova *et al.* [1,15].

We next perform an analysis of charge and spin density distribution in the fully optimized Rh-C<sub>60</sub> polymer with defects using the state-of-the-art *ab initio* computational methods. Three representative kinds of defects were studied in detail; namely the carbon adatoms, the mono-vacancies and the substitutional nitrogen impurities. In fig. 2a, we show the charge transfer that is induced by the carbon vacancies, while in fig. 2b we show the charge transfer that is developed if each monovacancy is replaced by a carbon adatom. In these figures, two striking features are evident. The first is that there is a depletion of electrons from each defect site (vacancy or adatom), resulting in it being positively charged. The second feature is that a charge density wave-like (CDW-like) disturbance develops around each defect which does not decay as one moves away from this region. This is because of a negative charge accumulation

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<sup>(1)</sup>The electronic band structure calculations use a *sp<sup>3</sup>s\** tight-binding model [16] that correctly reproduces the band gap for bulk carbon in the diamond and graphite phases. The band structure calculation has been performed within the spirit of our TBMD scheme using the experimental intra-atomic splitting value; it leads to a magnetic moment per atom of approximately 0.008  $\mu_B$  in good agreement with experiment [1].

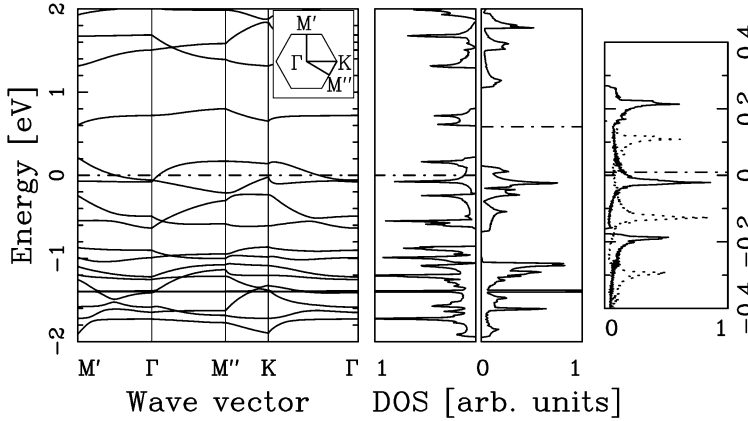


Fig. 1 – Band structure for the Rh-C<sub>60</sub> polymer with one vacancy per C<sub>60</sub> unit (left), density of states (DOS) (left of the middle panel) and DOS in the absence of any vacancy (right of the middle panel). The Fermi levels are indicated by dashed lines. The right panel shows DOS in the presence of vacancy for spin-up (solid line) and spin-down (dashed line), calculated for  $s_0 = 0.05$  eV [13].

at the atoms forming the inter-C<sub>60</sub> 2 + 2 cycloaddition bonds, facilitating a smooth joining with the CDW-like disturbance around the defect in the neighboring C<sub>60</sub> unit. No qualitative change in these features was found when the defect sites were changed arbitrarily. However, it was found that these features are more pronounced in the case of defects that lead to aligned delocalized  $p_z$  orbitals. Finally, substituting two carbon atoms neighboring one vacancy site or healing one of the vacancies with nitrogen atoms, no appreciable changes were found in the charge distribution of the corresponding systems with defects. However, the distinct feature related with the presence of the substitutional N-atoms is the delocalization of the spin density which (as discussed below) is localized by the vacancies or the adatoms. The accumulation of excess negative charge on the atoms forming the inter-C<sub>60</sub> link and similar but opposite charge on the defect sites gives rise to a rather large electric dipole moment (EDM) which is found to be of magnitude 3.32 and 2.26 debyes in the adatom and monovacancy cases, respectively. These results demonstrate a common role played by the two dissimilar defects in an otherwise periodic C<sub>60</sub>-polymer. In the case of a graphene layer, where there is an absence of negative charge accumulation, it was found that the positive charge disturbance decays away from the defect area. In this case the calculated EDM value is 0.39 debyes.

A spin density analysis of the relaxed system with the defect (vacancy or adatom) shows that any excess or deficiency in the total spin-densities are not found to be distributed similarly to the charge density. Instead, excess spin-densities appear concentrated around the defect sites in the right C<sub>60</sub> unit. These sites, thus, form the core-sites for the development of a magnetic phase. A further detailed analysis of our *ab initio* results reveals that the introduction of one defect per C<sub>60</sub>-unit leads to a global redistribution of electrons in the bonds resulting in eight of the carbon atoms becoming trivalent, while all the others remaining tetravalent. Half of the trivalent atoms appear in the immediate neighborhood of the vacancy sites while the other half are located outside their immediate neighborhood. Some of the trivalent atoms possess zero total charge and zero total spin creating, thus, an apparent inconsistency. Our results indicate that this seeming inconsistency can be understood because these atoms appear to develop a *remote delocalization* which extends over a small number of trivalent or tetravalent C-atoms. This type of delocalization, being different from the global delocalization found

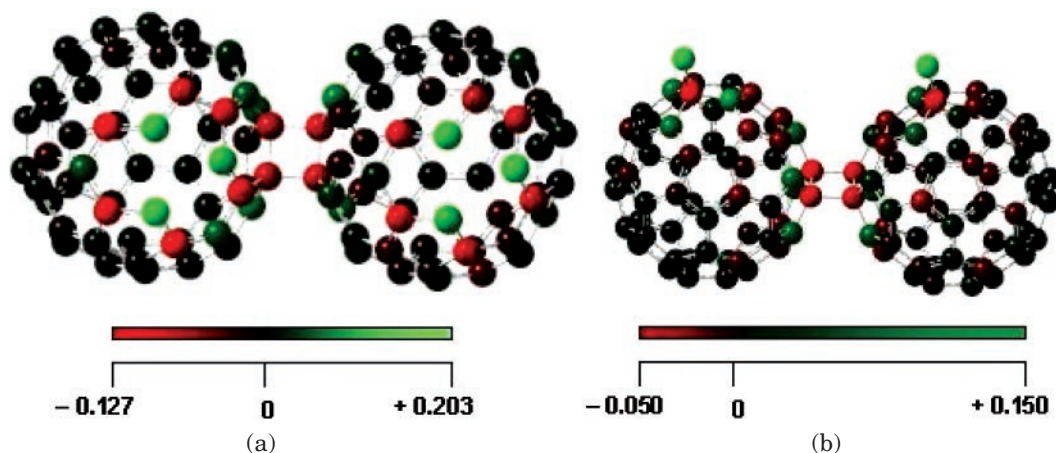


Fig. 2 – Figures showing the effect of charge transfer induced by (a) the vacancy and (b) the adatom (shown in green on-line) in the presence of 2+2 cycloaddition. The atoms surrounding the vacancy are positively charged while the atoms participating in the cycloaddition are negatively charged. Similarly, in (b), the adatoms are positively charged, while the atoms participating in the cycloaddition are negatively charged.

for the lone electrons in ref. [8], 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. It is this remote delocalization which, according to our results, develops the ferromagnetic coupling among the localized spins. In this view, it is worth noting that the substitutional N-atoms destroying the spin localization may lead to the passivation of ferromagnetism. This observation may explain the proposed selective passivation of the ferromagnetic pathways due to hydrogen in the  $C_{60}$ -polymers [9].

A careful observation of our results which emphasize the defect-related magnetism in the  $C_{60}$ -based polymers allows us to illustrate analogies with the magnetic mechanism in FM charge-transfer salts proposed by McConnell and known as the McConnell-II model [11, 12, 17, 18]. Specifically, in such systems, the possibility for a FM ground state arises when either the donor (D) or the acceptor (A) molecules exhibit triplet ground state. *I.e.* McConnell proposed that if an ionic charge-transfer pair ( $D^+A^-$ ) could be built that had a back charge-transfer excitation to a neutral triplet state instead of a singlet state (*i.e.*  $D^0$  is a triplet), then the  $D^+A^-$  pair could also be a triplet, due to the mixing of the charge-transfer state with the  $D^0A^0$  state. We show this schematically in fig. 3.

It should be noted that the kinetic exchange picture tacitly implies that the ground state is a superposition of the neutral and charge-transfer excited states. Thus, McConnell's approach is reminiscent of Van Vleck's [19] pioneering investigation on the origin of the *d-magnetism* in Ni and the other transition metals demonstrating, thus, that the ferromagnetism of the

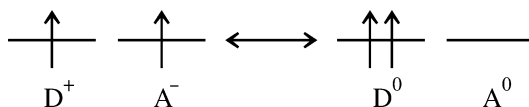


Fig. 3 – Schematic representation of charge-transfer mixing in McConnell's charge-transfer ferromagnet (McConnell-II model).

defected polymeric- $C_{60}$  has the same origin as the ferromagnetism of the  $3d$ -metals *i.e.*, the  $e$ - $e$  correlations [20].

A critical factor for the organic materials to become McConnell ferromagnets is, on the one hand, the creation and stabilization of generalized donor and acceptor sites in the material and, on the other hand, the creation of accessible interaction pathways which will ensure the development of a sufficient kinetic exchange. The latter is proposed to be the key factor for the development of ferromagnetic pathways in the  $C_{60}$ -polymers and in a class of defected materials (see below). These pathways appear as the result of electron correlations activated in the presence of defects. It is worth noting that the possibility of the mechanism of the configurational mixing to be a possible origin of the ferromagnetism of the V center in ionic oxides ( $BeO$ ,  $ZnO$ ,  $HfO_2$ , etc.) was suggested by Stoneham as early as in 1976 [21], and much later by other groups as well [17,18].

A donor-acceptor type magnetic material that can be characterized as a generalized-McConnell-II ferromagnet or, most importantly, demonstrates the common origin of  $sp$ - and  $d$ -magnetism [20] is the TDAE- $C_{60}$ . In this material, the defects may lead to spatial orbital ordering described in terms of the ground and lower excited states as modified by induced intra-molecular Jahn-Teller distortions and cooperative Jahn-Teller interactions [22].

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 [23] has demonstrated that Ca-vacancies create significant perturbations in the charge distribution of the defect-free material leading 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 [24], 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 FM  $C_{60}$  polymers. That is, both systems exhibit two kinds of defects which act as generalized donor and acceptor sites; they are just members of the same class of magnetic materials that can be characterized as ferromagnets of the generalized McConnell-II model. Furthermore, for both systems the development of a hydrogen-mediated spin-spin interaction has been suggested recently [9,25]. Other possible members of this class may be the hexaborides [26,27], the  $TiO_2$  in which Ti is partially replaced by Co [24,28], conjugated polymers [29]), etc.

In all these new magnetic materials, the generic nature of the defect-originated ferromagnetism becomes apparent. One may argue, however, that differentiations appear in the proposed models about the way the ferromagnetic pathways are developed. In this letter, on the one hand, it is emphasized that electron correlations as described within the kinetic exchange interaction do not only account for the source of the  $s$ - $p$  ferromagnetism but they can also describe it on the same footing as the  $d$ -ferromagnetism. On the other hand, the differentiations reported for the development of the suitable ferromagnetic pathways (or the FCMs) are considered as reflecting the physical processes in terms of which one can view the effect of the electron correlations; they are all consistent with the proposed generalization of McConnell's theory which appears as quite general. As that it unifies the magnetic behavior of some newly observed ferromagnets which, thus, can be classified as a wider class of magnetic materials.

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