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LETTER TO THE EDITOR

Are s–p- and d-ferromagnetisms of the same origin?**Antonis N Andriotis¹, R Michael Sheetz² and Madhu Menon^{2,3}**¹ Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, PO Box 1527, Heraklio, Crete, 71110, Greece² Center for Computational Sciences, University of Kentucky, Lexington, KY 40506-0045, USA³ Department of Physics and Astronomy, University of Kentucky, Lexington, KY 40506-0055, USA

E-mail: andriot@iesl.forth.gr, rmshee0@email.uky.edu and super250@pop.uky.edu

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Online at stacks.iop.org/JPhysCM/17/L35**Abstract**

The recent experimental discovery of ferromagnetism in organic C₆₀-based polymers has re-ignited interest in the topic of magnetism in organic and non-traditional inorganic materials. While the nature of the s–p magnetism of C₆₀-based polymers has some unique features not shared with non-traditional inorganic materials, a defect-based picture of the magnetism is found to provide a common thread in these materials. By analysing the common features seen in the magnetic properties of various types of unconventional systems we show that the magnetism in these materials can be considered as a generalized form of the well known McConnell ferromagnetism and that it has common origins with the traditional ferromagnetism of the transition metal systems.

Recently, there has been an increase in the works reporting the exotic s–p type of magnetism which has been observed and/or predicted in organic materials (such as, for example, C₆₀-based polymers [1], tetrakis-dimethyl-amino-ethylene–C₆₀ (TDAE–C₆₀) [2, 3], p–nnn radicals [4–6]), planar conjugated π -hydrocarbon systems [7, 8] and some non-traditional inorganic materials (such as, for example, CaO [9], ZnO [10], TiO₂ [11, 12], hexaborides [13, 14]). Interestingly, an in-depth study of these materials has shown that they exhibit several common features, such as the presence of structural and/or topological defects, the development of significant charge transfer, the existence of a degenerate ground state and, in some cases, a resonant ground state [15, 16]. A more detailed examination of the results emphasizing the defect-related magnetism in the C₆₀-based polymers allowed us to elucidate the underlying mechanism giving rise to the magnetism in these materials and to draw analogies with the magnetic mechanism proposed by McConnell for the ferromagnetic charge-transfer salts and known as the McConnell-II model [17–19]. It should be recalled that the McConnell-II model predicts that an 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 ferromagnetic (FM) ground state if either

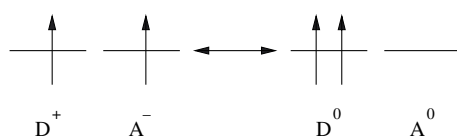


Figure 1. Schematic representation of charge-transfer mixing in McConnell's charge-transfer ferromagnet (McConnell-II model).

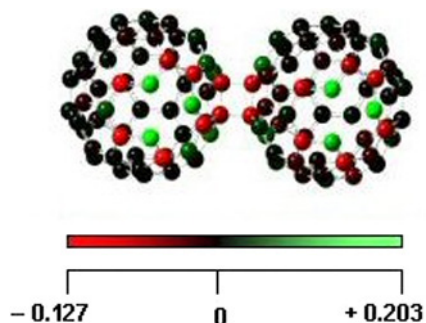


Figure 2. Figure showing the effect of charge transfer induced by the vacancy and the presence of 2 + 2 cycloaddition. The atoms surrounding the vacancy are positively charged while the atoms participating in the cycloaddition are negatively charged. (This figure is in colour only in the electronic version)

the donor or the acceptor molecule have a triplet neutral ground state (shown schematically in figure 1). 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.

We have recently demonstrated [16] that the existence of the 2 + 2 cycloaddition [20] bonds (which provide sp^3 -bonded carbon atoms) in coexistence with vacancies can explain the origin of the magnetism in polymerized- C_{60} materials [1]. In particular, we have shown that the vacancies and the 2 + 2 cycloaddition bonds provide the necessary unpaired electrons, while also initiating the charge-transfer processes (see figure 2) which create and sustain large electric dipole moments. The latter develop the necessary ferromagnetic coupling mechanism (FCM) among the unpaired spins and lead to the development of an FM state. In such a mechanism, the electron–electron ($e-e$) correlations play a crucial role as they promote the high spin multiplicity states and make them energetically more favourable as a result of the kinetic exchange interaction rather than the exchange interaction. The magnetic picture induced by the interplay between the vacancies and the cycloaddition bonds is not affected if the site of vacancies is changed arbitrarily. But more importantly, we have also found that the presented defect origin of magnetism is rediscovered if, in our model calculations, each vacancy is substituted by another kind of defect, namely, a carbon adatom adsorbed on each C_{60} at an arbitrary site. Due to the fact that the 2 + 2 cycloaddition bonds gain electron charges while the vacancy regions lose electrons, in analogy with the McConnell model, the vacancies can be assigned to play the role of the donor molecules and the 2 + 2 cycloaddition bonds to 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 favourable ground state. In this view, the defect magnetism of C_{60} -based polymers can be considered as a generalization of the McConnell-II model. Similarly, the ZnO system which is simultaneously doped by Co^{2+} and Cu^+ ions and includes a small concentration of Zn vacancies is in complete analogy with the ferromagnetic C_{60} polymers⁴. That is, both are charge-transfer systems exhibiting two kinds of defects which act as donor and acceptor sites [21].

Other donor–acceptor type magnetic materials which can be classified as generalized McConnell-II ferromagnets may include the following charge-transfer systems [21]: TDAE–

⁴ When Co is substituted for Zn in ZnO it appears as Co^{2+} ion. In the presence of Zn vacancies the charge state of Co becomes $Co^{1.6+}$ [10]. No reference is currently available on the charge state of Co in the presence of Cu^+ .

C₆₀ [2, 3], TiO₂ in which Ti ions are partially substituted by Co ions [11, 12], doped CaO [9], doped hexaborides [13, 14], etc. For each of these materials there are theoretical reports predicting the existence of a ferromagnetic ground state. In some of the cases these predictions have been verified by recent experimental results. Thus, concurrently with our defect-related model for s–p magnetism, 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) [9]. Furthermore, defect-based models such as, for example, the orbital ordering model [2, 22] and the excitonic model [23, 24], have been proposed to explain the unusual s–p-ferromagnetism. In some other theoretical models, the presence of defects is identified as the source responsible for providing the unpaired electron spins, while the traditional *super-exchange* or the *s–d coupling* is assumed to provide the FCM [9]. There also appear attempts to explain the s–p magnetism in terms of the carrier-induced magnetic theory. In this approach, the hopping of carriers among the impurity sites causes the FM ordering of the localized spins through the double-exchange mechanism [25]. Finally, in some reports the s–p magnetism of some particular systems is considered as a demonstration of the flat band ferromagnetism [26, 27]. These studies have demonstrated that the above-mentioned systems are highly correlated and their observed ferromagnetism is the outcome of the e–e correlations as these are developed in the specific geometric configuration of the system and the presence of defects.

It is worth noting that the various formalisms used to implement the e–e correlations, i.e., the s–d coupling, the *kinetic exchange interaction*, the orbital ordering and the excitonic models, denote expressions related to the description of the level (approximation) and the way (i.e., the technical implementation) the e–e correlations are treated in each of the above described methods. Therefore, they can be understood as complementary descriptions of the same underlying physics. In particular, it can be observed that all the formalisms referred to in the above follow the same fundamental approach in incorporating the e–e correlations. That is, they express the ‘correlated’ wavefunctions as a superposition of Slater determinants including different classes of molecular orbitals (MOs) of lowest excited and/or resonant states. For example, the polarization of the electron gas in the presence of a localized magnetic moment (inherent to the s–d coupling) can be described as a superposition of ‘uncorrelated’ wavefunctions as dictated by the second order perturbation theory. The organic McConnell ferromagnets, on the other hand, are described by a superposition of neutral and charge-transfer MOs; the spatial orbital ordering systems are 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].

These implementations of the e–e correlations are reminiscent of Van Vleck’s [28] pioneering investigation on the origin of the *d-magnetism* in Ni and the other transition metals. Van Vleck, employing a superposition of charged states as these were dictated by the Heisenberg and the Stoner–Wohlfarth models, was able to study the energetics of these popular magnetic models for the transition metals. The key factors in the determination of the energetics of these two models were the presence of charge transfer, the exchange electron energy attributed to intra-atomic processes [29], and the connection of the latter with the existence of degenerate electron states [28]. The similarities of these key factors with the common features exhibited by the s–p ferromagnets mentioned in the above are quite striking.

Much later, Roth [30], based on Van Vleck’s observation that *the presence of orbital degeneracy is important in the occurrence of ferromagnetism*, demonstrated that this is, in fact, possible for a narrow d-band Hubbard model [31] with two degenerate orbital states at half filling. For this model Roth showed that a spatial ordering of the orbitals is energetically favourable in the form of two sublattices each with predominantly one of the orbital states and for the spins to line up ferromagnetically. This model was exploited recently by Kawamoto [22]

in an effort to explain the ferromagnetism in TDAE-C₆₀. This is just an excellent example that points to the common origin of the s-p- and the d-magnetism. The same conclusion can also be arrived at by comparing McConnell's and Van Vleck's implementation of the e-e correlations.

These observations demonstrate the common origin and the common features that exist between the newly observed s-p magnetism and the usual d-magnetism. Charge-transfer processes and orbital degeneracy seem to be the key factors. However, the charge-transfer processes have to be large enough in order to develop and sustain strong fields that can provide the necessary kinetic exchange interaction for promoting the high spin states as the favourable ground states. The latter seems to be better demonstrated in the newly discovered s-p magnetism. On the other hand, the differentiation between the two types of magnetism that has appeared in the literature in the form of various models reflects the leading terms that are kept in the implementation of the e-e correlations and the underlying physical picture of such an approximation.

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