

Spin-transfer mechanism of ferromagnetism in polymerized fullerenes: *Ab initio* calculationsO. E. Kvyatkovskii,^{1,*} I. B. Zakharova,² A. L. Shelankov,^{1,3} and T. L. Makarova^{1,3}¹*Ioffe Physico-Technical Institute of the RAS, St. Petersburg, 194021, Russia*²*State Polytechnic University, St. Petersburg, 195251, Russia*³*Umeå University, 90187 Umeå, Sweden*

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A mechanism of the high-temperature ferromagnetism in polymerized fullerenes is suggested. It is assumed that some of the C_{60} molecules in the crystal become magnetically active due to spin and charge transfer from the paramagnetic impurities (atoms or groups), such as hydrogen, fluorine, hydroxyl group OH, amino group NH_2 , or methyl group CH_3 , dispersed in the fullerene matrix. The exchange interaction between the spins localized on the magnetically active fullerenes is evaluated using *ab initio* calculations. The nearest neighbor and next nearest neighbor exchange interaction is found to be in the range 0.1–0.3 eV, that is, high enough to account for the room temperature ferromagnetism.

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I. INTRODUCTION

Recent developments in material science have resulted in the discovery of a novel class of magnetic organic materials based on carbon such as fullerenes^{1–10} and graphite.^{11,12} Fullerene C_{60} intercalated with the organic TDAE molecule is ferromagnetic below 16 K.^{1,3} The ferromagnetic ordering below ≈ 370 K in the PVDF- C_{60} composite, where PVDF is polyvinylidene fluoride, $(-CH_2-CF_2-)_n$, has been reported.² More recently, room temperature ferromagnetism has been reported in fullerenes polymerized by means of photoprocesses^{4–6} and by high pressure–high temperature treatment,^{7–10} and hydrofullerites.¹³ In the present paper, we focus our attention on the problem of the high-temperature magnetism in polymerized fullerenes.

In accordance with the band structure calculations, an ideal lattice of polymerized fullerenes¹⁴ is not expected to show magnetism. Some yet unidentified structural or chemical imperfections are of crucial importance for the fullerenes to become magnetic. The data suggest that the type of polymerization, rhombohedral,^{7–9} or tetragonal,^{10,15} is not of primary importance, and that the polymerization is necessary but not sufficient a condition for a high temperature ferromagnetism. For photopolymerized fullerenes, the presence of oxygen is a prerequisite.^{4–6} The results of the Ref. 2 give the hint that C_{60} radical adducts, $C_{60}R_n$, where R originate from the organic polymer fragments, are responsible for the magnetism. Seeing that the intrinsic magnetism in polymerized fullerenes remains an experimentally controversial issue,^{15–17} it is of interest to demonstrate that high-temperature magnetism is a theoretically feasible possibility in realistic assumptions about the materials.

To answer the question about a microscopic origin of the ferromagnetism in carbon-based materials, the theory has to find the structural element of the carbon matrix that carries unpaired spins, and to show that the interaction between the spin of the units leads to a parallel spin alignment. So far, the theoretical development has been in the picture of magnetically active structural defects, i.e., defects with localized spins, interaction of which is mediated by the magnetically passive carbon matrix.^{18–24} Defects of different complexity

and topology were considered: carbon vacancies in graphite,^{18,19} carbon adatoms on the graphene layer,²⁰ vacancies in the fullerene cages,²¹ partially opened intermediate fullerene cage structures with the zigzag-type edge,²² the carbon tetrapods with negative Gaussian curvature,²³ and the special open-cage defect structure with the hydrogen atom bonded chemically to one of defect carbon atoms.²⁴ It is yet unclear whether these defects are present in real fullerene samples (see, however, Ref. 25, where atomic-scale defects were observed in graphene layers) and whether the spin-spin interaction is ferromagnetic and strong enough to account for the high-temperature magnetism of polymerized fullerenes.

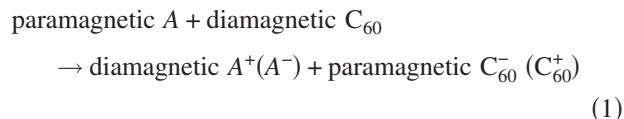
As pointed out in Ref. 24, in the periodic version of the defective structure of Rh- C_{60} proposed in the Ref. 21, i.e., in Rh- C_{59} , the interaction between the magnetic moments localized on the cages is not ferromagnetic. The defective structure model proposed in Ref. 24 does provide a mechanism for ferromagnetic ordering, but the computed energy difference between ferromagnetic and antiferromagnetic states is too small (3 meV per cage) to explain the high-temperature magnetism. Besides, the magnetically active structural defects approach is hardly applicable to cold-polymerized fullerenes^{2,4–6} where the formation of C_{60} cage defects is ruled out. A model, where magnetism arises in a system of undamaged fullerenes, has been suggested in Ref. 26. In accordance with the calculations, a neutral C_{60} dimer turns into the triplet state provided the interfullerene bond is shortened below the critical length 1.3 Å.²⁶ This value is appreciably smaller than the experimentally observed bond length 1.58–1.62 Å, and an enormous pressure would be needed to decrease the intermolecular distance below the critical one. It is not clear whether the model is universal, in particular in the view of the observation that the magnetic transition may take place even without any external pressure.^{1,2,4–6}

In this paper we suggest a scenario where doping creates fullerene radical adducts $C_{60}R$, i.e., paramagnetic species with unpaired spins localized on fullerenes. In our model, ferromagnetism occurs in a network of the paramagnetic species dispersed in a polymerized fullerene matrix. The model is based on the computational observation²⁷ that the ground state of a doubly charged $[2+2]$ cycloadduct dimer $(C_{60}^\pm)^2$ is triplet,²⁷ with the singlet state separated by the gap of order

of 0.2–0.3 eV.²⁸ In other words, the spins localized on the neighboring C_{60}^{\pm} ions interact ferromagnetically, and the interaction is strong enough to account for the high-temperature ferromagnetic transition in polymerized fullerenes.

In our model we assume that some of the C_{60} molecules in the crystal initially spin inert and charge neutral, become magnetically active (paramagnetic) due to the charge transfer from radicals (impurities), naturally accompanied by the spin transfer. Although the electron transfer is the actual reason for the fullerenes to acquire spin, we label the scenario “spin transfer” because C_{60} acquires spin $\frac{1}{2}$ for any direction—to or from the C_{60} molecule—of the electron transfer. The purpose of this paper is a detailed study of the spin transfer model using first principle calculations.

The present mechanism is best illustrated by the case of a paramagnetic impurity A (A =alkali metals, hydrogen, fluorine, the hydroxyl group OH, amino group NH_2 , methyl group CH_3 , etc.) allowing for the charge-spin transfer reaction



with the formation of charged paramagnetic ions C_{60}^{\pm} . Here we speak about the final states of the charged impurity or fullerene, with particular emphasis on their spin states. One can see that our scenario has many features in common with the charge transfer complexes model³ proposed for the description of magnetic properties of TDAE- C_{60} and to the qualitative picture of paramagnetic (open shell) C_{60} radical adducts considered responsible for the ferromagnetism in C_{60} dispersed in PVDF.²

In the model under consideration, the primary source of the local spin moments is the radical impurities dispersed in the fullerene lattice. In this respect, the spin transfer magnetism in polymerized C_{60} is akin to the ferromagnetism in a dilute system of magnetic atoms in an insulator or semiconductor, with some important differences however. First, the reaction Eq. (1) transforms paramagnetic impurity atom (or molecule) to a *diamagnetic* ion with closed electron shells. This means that the impurities, nominally paramagnetic, play only a passive role in our scenario of the sources of net charges and spins. Second, both magnetically active centers (actual paramagnetic species) and magnetically passive ones (diamagnetic matrix) are constructed from the fullerene molecules.

To validate our physical picture of magnetism, we evaluate the coupling between paramagnetic species (nearest neighbors and next nearest neighbors) in the polymerized fullerene matrix. The role of the fullerene radical adducts, $C_{60}R$, where $R=H, F, OH, NH_2, \text{ or } CH_3$, in the formation of the ferromagnetic ground state is studied. For this purpose, the first-principles cluster calculations of the electronic structure, optimized geometry, and energies of the two low-lying levels corresponding to the singlet and triplet spin states for the pairs of ions C_{60}^{\pm} and C_{60} radical adducts, $C_{60}R$ ($R=H, F, OH, NH_2, CH_3$) connected by [2+2] cycloaddition

of “66” bonds are carried out. To inspect the range of the exchange interaction, similar calculations are performed for the pair of $C_{60}H$ radical adducts occupying the opposite (next nearest) vertexes of the tetragonal tetramer $(C_{60})_4H_2$, which is a doped fragment of the 2D (two-dimensional) polymerized tetragonal phase of C_{60} .²⁹

The calculations have been carried out in the framework of the density functional theory (DFT) and *ab initio* Hartree-Fock (HF) methods. In the DFT calculations, the hybrid functional of Becke^{30–32} (B3LYP) was employed, which includes the gradient-corrected exchange and correlation functionals along with the exact exchange. The HF calculations were carried out using the PC GAMESS version³³ of the GAMESS (US) QC package.³⁴ The DFT calculations were carried out using the PC GAMESS (Ref. 33) and the GAUSSIAN 03 suite of programs.³⁵ We exploited the spin-unrestricted method for both singlet and triplet spin states. The Gaussian basis sets employed are 3-21G and 6-31G*. The energy gradient convergence tolerance was less than 10^{-4} a.u.

Recently, the B3LYP method has been successively applied to solids.^{36–41} A significant improvement over the LDA results for electronic, structural, and vibrational properties for some semiconductors and insulators has been achieved by this method.^{36–38} In addition, the B3LYP method improves the magnetic moments and energy gaps, and correctly predicts the ground state for some antiferromagnetic insulators.^{39–41} For the random impurity distribution case, the cluster approach is more appropriate than methods developed for periodic systems.

The paper is organized as follows. In Sec. II we consider a dimer as the smallest nontrivial fragment of the lattice. We study the charge and spin distributions in the doubly charged dimer $(C_{60})^{\pm 2}$ and calculate the exchange interaction of the spins localized on the fullerenes in the dimer. In Sec. III, we consider spin properties of dimers “doped” with radicals. To estimate the range of the exchange, we consider in Sec. III a cluster with four fullerenes and calculate the next nearest neighbor exchange interaction. In Sec. IV we discuss the results and estimate the Curie temperature in our model.

II. CHARGED DIMER: THE EXCHANGE INTERACTION

The rhombohedral (Rh) and tetragonal (Tg) polymerized C_{60} crystals are built of C_{60} layers in which fullerene molecules are connected by [2+2] cycloaddition of “66” bonds.^{29,42} The smallest lattice fragment is two adjacent C_{60} molecules, a dimer, and we begin our study with the analysis of this simplest system in its neutral and charged states.

It is known from the literature that the ground state of a free fullerene dimer radical adduct $R-C_{60}-C_{60}-R$ is a singly bonded isomer with the radicals R placed in specific positions.⁴³ The transition from the [2+2] double bond isomer to the singly bonded one requires breaking of one of the bonds and a rotation of the fullerene around the remaining bond. This process may occur in a metastable dimer phase,⁴³ but in a polymeric fullerene network, where the molecules are tightly bound with the nearest neighbors, the rotation costs the bending and torsion energy and is, therefore, unfea-

TABLE I. The total energies, lengths, and orders of the interfullerene bonds for D_{2h} isomer $(C_{60})_2^{2-}$ in the singlet and triplet states for the optimized structure calculated by the use of the UB3LYP hybrid DFT method with the 3-21G and 6-31G* basis sets employed.

| Basis set Spin state | 3-21G | | 6-31G* | |
|-------------------------|-----------|-----------|-----------|-----------|
| | Singlet | Triplet | Singlet | Triplet |
| Total energy (a.u.) | -4547.166 | -4547.175 | -4572.430 | -4572.442 |
| Bond length (Å) | 1.593 | 1.597 | 1.597 | 1.593 |
| Bond order | 0.799 | 0.796 | 0.859 | 0.864 |

sible. Thus, we assume that the charge and spin transfer from impurities to fullerene molecules take place without changing the bonding type. Therefore, we study a doubly charged [2+2] cycloadduct isomer $(C_{60})_2^{2\pm}$ as a fragment of the doped polymerized fullerene lattice.

To obtain a quantitative information on the spin and bonding configuration, we have performed spin-unrestricted B3LYP (UB3LYP) calculations of the electronic structure, the total energy, and optimized geometry for the charged $(C_{60})_2^{2\pm}$ dimer in the state with the total spin $S=0$ (singlet) and $S=1$ (triplet).

To check our methods, we began our calculation with the case of a neutral dimer. In agreement with earlier results,⁴⁴ we found the [2+2]-cycloadduct isomer singlet with D_{2h} symmetry to be the lowest energy state of $(C_{60})_2$. A triplet state of the doubly bonded neutral dimer lies 2.1 eV higher in energy. In the singlet state, the doubly charged [2+2] cycloadduct isomer has D_{2h} symmetry.⁴⁴ The symmetry of the triplet states has not, to our knowledge, been studied before. We have considered the dimer in triplet state possessing one of the two simplest symmetry elements: inversion, C_i , symmetry and the mirror, C_s , symmetry with the plane of symmetry transverse to the dimer axis. The B3LYP calculations give identical results for the triplet states of both C_i and C_s isomers, and show that the ground state of the [2+2] cycloadduct $(C_{60})_2^{2\pm}$ dimer is the D_{2h} isomer in the triplet spin state.

Listed in Tables I and II, the results of the B3LYP/6-31G* calculations for both negatively charged $(C_{60})_2^{2-}$ and positively $(C_{60})_2^{2+}$ charged dimers show that the

TABLE II. The total energies, lengths, and orders of the interfullerene bonds for D_{2h} isomer $(C_{60})_2^{2+}$ in the singlet and triplet states for the optimized structure calculated by the use of the UB3LYP hybrid DFT method with the 3-21G and 6-31G* basis sets employed.

| Basis set Spin state | 3-21G | | 6-31G* | |
|-------------------------|-----------|-----------|-----------|-----------|
| | Singlet | Triplet | Singlet | Triplet |
| Total energy (a.u.) | -4546.434 | -4546.442 | -4571.765 | -4571.772 |
| Bond length (Å) | 1.584 | 1.602 | 1.581 | 1.597 |
| Bond order | 0.806 | 0.791 | 0.874 | 0.859 |

TABLE III. Effective exchange integral $J=(E_{\uparrow\downarrow}-E_{\uparrow\uparrow})$ for pair of adjacent C_{60}^{\pm} ions in polymerized fullerene. The energies $E_{\uparrow\downarrow}$ and $E_{\uparrow\uparrow}$ are total energies of low-lying singlet and triplet states for corresponding [2+2] cycloadduct charged D_{2h} isomers

| Method | J (eV) | |
|--------------|-------------------|-------------------|
| | $(C_{60})_2^{2-}$ | $(C_{60})_2^{2+}$ |
| AM1 | 0.52 | 0.45 |
| B3LYP/3-21G | 0.12 | 0.10 |
| B3LYP/6-31G* | 0.16 ^a | 0.10 |

^aThe *ab initio* Hartree-Fock/6-31G* calculations give in this case the value equal to 0.72 eV.

ground state of a doubly charged [2+2]-cycloadduct isomer is the triplet spin state of the D_{2h} symmetry. It is interesting that the properties of the negatively (“electron doped”) and positively (“hole doped”) charged dimers are rather close, as seen from the comparison of Tables I and II. Also, one sees from Tables I and II that the results obtained at 3-21G and 6-31G* levels are in close agreement.

To identify the nature of the stationary points on the potential energy surface (a true minimum or a saddle point), we calculated the vibrational frequencies for the neutral singlet D_{2h} $(C_{60})_2$ isomer and for both the singlet and triplet D_{2h} $(C_{60})_2^{2\pm}$ isomers. The absence of imaginary vibrational frequencies indicates that all the stationary points are minima. A robust feature seen from the *ab initio* dimer calculations is that the bridging bonds of the [2+2] cycloadduct are not affected by doping and are almost impenetrable for the spin. In other words, each fullerene in a charged dimer possess a well defined spin localized on the fullerenes. Hence, one can conveniently describe the interacting pair in terms of the Heisenberg Hamiltonian⁴⁵

$$H = -2JS_1 \cdot S_2, \quad (2)$$

where S_i ($S^2 = \frac{3}{4}$) is the spin vector on the i th site of the dimer and J is the corresponding exchange integral. The latter can be presented as

$$J = (E_{\uparrow\downarrow} - E_{\uparrow\uparrow})/2, \quad (3)$$

where $E_{\uparrow\downarrow}$ and $E_{\uparrow\uparrow}$ are the energies of the dimer in the singlet and triplet states, respectively.

We calculate the exchange integral J , from the singlet-triplet splitting Eq. (3), having taken the corresponding energies from Tables I and II. The results are listed in Table III. For all the calculation methods we obtained a positive exchange integral, i.e., the interaction between the spins localized on the adjacent fullerenes is ferromagnetic. Both spin-unrestricted and spin-restricted B3LYP calculations give the same value of the singlet state energy and, therefore, the singlet spin state is not antiferromagnetic by its nature. Note that both the semiempirical AM1 and *ab initio* Hartree-Fock methods, where correlation effects are ignored, noticeably overestimate J . The B3LYP hybrid functional calculations, which take the electron correlations into account along with the exact exchange, are more accurate and reliable; they give

far lower values of the exchange integral: $J=0.16$ eV for $(C_{60})_2^{2-}$ and 0.10 eV for $(C_{60})_2^{2+}$.

This is the key result supporting our model of ferromagnetic fullerenes: In all the studied cases of the [2+2] cycloadducts $(C_{60})_2^{2\pm}$, the exchange integral is invariably positive and the exchange interaction is rather strong. We emphasize that the ferromagnetic exchange is an intrinsic property of polymerized [2+2] cycloadduct fullerenes.

We note also that the spin inter cage interaction is more sensitive to the relative orientation of the fullerenes than to the inter cage separation: We see from *ab initio* calculations that for the relative orientation which corresponds to a *singly* bonded dimer, the separation is almost the same as in the [2+2] cycloadduct case, but the ground state for the singly bonded isomer $(C_{60})_2^{-2}$ is different: It is spin singlet separated from the triplet state by the gap ~ 0.7 eV at the B3LYP/3-21G level.

III. EXCHANGE INTERACTION FOR RADICAL ADDUCTS $C_{60}R$

Most important question is the availability of impurities with the wanted property to create spins localized on fullerenes in the polymerized matrix. Two types of doping can be envisaged, depending on the impurity character. The first one is a charged complex formed in the fullerene matrix, comprising a fully ionized impurity bound primarily by the Madelung electrostatic forces (ionic limit). This is the case, for example, in TDAE- C_{60} , as well as for the alkali metal doping. Second, an impurity atom or molecule forms C_{60} radical adduct covalently bound with a carbon atom of the C_{60} cage (covalent limit). This is the case, for example, for hydrogen, fluorine, hydroxyl group OH, amino group NH_2 , or methyl group CH_3 .

We will focus our attention on the covalently bounded radicals (ligands) and especially on hydrogen. Particular interest in hydrogen doping stems from the fact that hydrogen, a donor, is always present in fullerene solids in noticeable amounts. Hydrogen was detected in rather large concentration (about one hydrogen atom per six fullerene molecules) in ferromagnetic samples of pressure-polymerized fullerene.²⁴ Fluorine is of general interest for it is one of the very few atoms that has stronger acceptor properties than C_{60} . Hydroxyl, amino, and methyl groups exemplify simplest molecular radicals.

We begin with the presentation of our results concerning the electronic structure of the above radical adducts. The spatial distribution of the Milliken atomic charge and atomic spin for $C_{60}H$ and $C_{60}F$ calculated at B3LYP/3-21G level is presented in Fig. 1.

Atomic Milliken charges (the sum of the atomic Milliken charges in the case of fullerene molecule), reflect the nature of the chemical bond, i.e., the degree of hybridization of the valence orbitals of the fullerene and impurity atoms, rather than the values of atomic net charges. The net charges are closely related to the spin density distribution. For $C_{60}H$ and $C_{60}F$, the B3LYP/3-21G calculations show that the Milliken charges of H and F are equal to 0.27 and -0.25 , correspondingly, whereas the atomic spin populations for both H and F

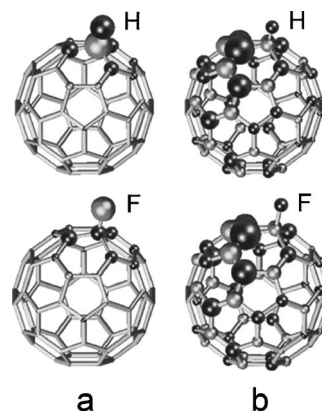


FIG. 1. The charge (a) and spin (b) density spatial distribution (Milliken atomic charges and spins) of the doped fullerenes $C_{60}H$ and $C_{60}F$. Black (gray) corresponds to positive (negative) charge or up (down) spins. The volume of the spheres is proportional to the absolute value of the corresponding variable on a given atom.

atoms are equal to 0.042. The latter values imply that the net charges for H and F are equal to ± 0.958 , respectively, and corresponding C_{60} net charges are equal to ∓ 0.958 . For comparison, sums of atomic spin populations for hydroxyl group OH, amino group NH_2 , and methyl group CH_3 are equal to 0.043, 0.072, and 0.042 respectively, that is much less than unity as for H and F, whereas corresponding sums of Mulliken atomic charges are equal to -0.16 , -0.03 , and 0.15.

To estimate the exchange interaction between the spins on neighboring fullerenes in the matrix, we have performed B3LYP/3-21G calculations for the cases of doped [2+2] cycloadduct dimers $H-C_{60}=C_{60}-H$ and $F-C_{60}=C_{60}-F$, $OH-C_{60}=C_{60}-OH$, $NH_2-C_{60}=C_{60}-NH_2$, $CH_3-C_{60}=C_{60}-CH_3$, as well as for a combination of donor and acceptor $H-C_{60}=C_{60}-F$ and $H-C_{60}=C_{60}-OH$. Several configurations differing in the initial position of the ligands relative to the fullerene molecules have been considered. For all of the configurations, the spins on the neighboring fullerenes are parallel in the ground state, forming a triplet, and the energy differences $E_{\downarrow\downarrow}-E_{\uparrow\uparrow}$ are of the order of several tenths of eV. The triplet-singlet splittings for the configurations shown in Fig. 2 are listed in Table IV.

The spatial distributions of the charge and spin density for doped dimers $R-C_{60}=C_{60}-R'$ (with $R, R'=H, F$) are shown in Fig. 2. The spin density, Fig. 2(b), is spread across the fullerenes, repeating the net charge density profile. Comparing Fig. 2 and Fig. 1, one concludes that in the dimer case, the spin distribution is nearly the same as for an isolated $C_{60}R$. Note that the spin density distribution is insensitive to the sign of the fullerene charge. Also, the spin and net charge distributions are insensitive to the choice of the radical: Our numerics shows that for $R-C_{60}=C_{60}-R$, $R=OH$, NH_2 , CH_3 , the spatial distributions of the net charge and spin density over the fullerene molecules are very similar to those in Fig. 2.

Remarkably, the spin density is zero on the bonds bridging the molecules, so that one can assign a spin to each of the fullerenes. This corresponds to the picture where the spin of an individual charged (doped) molecule is well defined, and

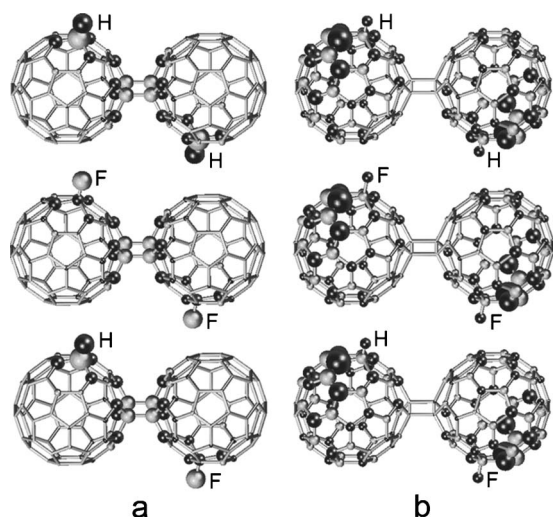


FIG. 2. The charge (a) and spin (b) density spatial distribution (Milliken atomic charges and spins) of the doped CA dimers $(C_{60}H)_2$, $(C_{60}F)_2$, $(C_{60})_2HF$. Black (gray) corresponds to positive (negative) charge or up (down) spins. The volume of the spheres is proportional to the absolute value of the corresponding variable on a given atom.

C_{60} molecules play the role of the sites on which spins reside. From Table IV, the nearest neighbor exchange interaction Eq. (3) is rather strong, $J \approx 0.3$ eV.

To estimate the spatial range of the exchange interaction, we consider a pair of fullerene hydrogen adducts $C_{60}H$ placed in the next nearest neighbors positions. For this, we compute properties of planar tetragonal tetramer $(C_{60})_4H_2$ (Fig. 3) with doped C_{60} at the opposite corners of the tetramer. The UB3LYP/3-21G calculations of the electronic structure and the total energy have been carried out for optimized geometry of the singlet and triplet spin states of the cluster. The singlet-triplet splittings are presented in Table IV. The charge and spin density spatial distributions for the tetramer $(C_{60})_4H_2$ displayed in Fig. 3 are very similar to that

TABLE IV. Total energies for the singlet, $E_{\uparrow\downarrow}$, and triplet, $E_{\uparrow\uparrow}$, states, and energy gain of spin polarized state, $E_{\uparrow\downarrow} - E_{\uparrow\uparrow}$, calculated at the UB3LYP/3-21G level for a number of doped [2+2] cycloadduct $R-C_{60}=C_{60}-R'$ dimers and for planar tetragonal tetramer $((C_{60})_4H_2)$.

| Doped isomer | $E_{\uparrow\downarrow}$ (a.u.) | $E_{\uparrow\uparrow}$ (a.u.) | $E_{\uparrow\downarrow} - E_{\uparrow\uparrow}$ (eV) |
|---------------------------|------------------------------------|----------------------------------|---|
| $H-C_{60}=C_{60}-H$ | -4548.182 | -4548.203 | 0.58 ^a |
| $F-C_{60}=C_{60}-F$ | -4745.555 | -4745.578 | 0.61 |
| $H-C_{60}=C_{60}-F$ | -4646.869 | -4646.890 | 0.56 |
| $OH-C_{60}=C_{60}-OH$ | -4697.751 | -4697.773 | 0.59 |
| $H-C_{60}=C_{60}-OH$ | -4622.967 | -4622.988 | 0.58 |
| $NH_2-C_{60}=C_{60}-NH_2$ | -4658.246 | -4658.268 | 0.58 |
| $CH_3-C_{60}=C_{60}-CH_3$ | -4626.393 | 4626.414 | 0.57 |
| $(C_{60})_4H_2$ | -9095.234 | -9095.259 | 0.68 |

^aThe B3LYP/6-31G* calculations give in this case the value equal to 0.57 eV.

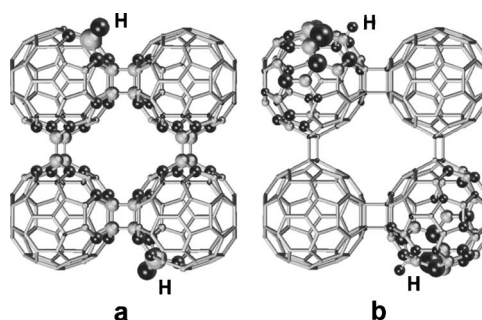


FIG. 3. The charge (a) and spin (b) distribution in the triplet spin state of the doped CA tetramer $(C_{60})_4H_2$. Black (gray) corresponds to positive (negative) charge or up (down) spins. The volume of the spheres is proportional to the absolute value of the corresponding variable on a given atom.

for the dimer in Fig. 2. The singlet-triplet splitting is positive (ferromagnetic) and close to that in a dimer. Therefore, we observe that the exchange interaction between fullerene radical adducts in a 2D layer does not fall within the two first coordination spheres. Moreover, the indirect exchange interaction mediated by fullerene matrix is somewhat stronger than direct one. Thus, it is very likely that the spin interaction extends far beyond the nearest neighbors, keeping its sign and magnitude. Of course, additional calculations of spin interaction between distant fullerene radical adducts in a large fragments of the lattice are needed to support this conjecture.

In conclusion of this section, we emphasize that the ferromagnetic exchange is an intrinsic property of polymerized [2+2] cycloadduct fullerenes rather than the radical impurity that makes the fullerene magnetically active.

IV. DISCUSSION AND CONCLUSIONS

Based on the presented *ab initio* calculations, the following physical picture emerges. Chemically pure polymerized fullerene lattice, rhombohedral or tetragonal, is a diamagnet with zero spin on the sites of the C_{60} matrix. Doping with radicals initiates reaction Eq. (1), and some of the sites of the matrix become paramagnetic as the result of the spin (and charge) transfer from the radical attached to the corresponding fullerene. The calculations of the spin distribution on the doped dimers and tetramers show that the spin transferred from the radical is smeared over the fullerene's surface, but it avoids the [2+2] four-membered rings connecting C_{60} 's, so that the transferred spin is well localized on the fullerenes. One comes to the picture of immobile spins occupying sites of the fullerene matrix.

The interaction of the localized spins can be described by the standard Heisenberg Hamiltonian. In accordance with our calculations, the Heisenberg exchange integral J is ferromagnetic and rather strong, $J=0.1-0.3$ eV. The cluster calculations in Sec. III, give the evidence that the ferromagnetic exchange extends at least to the next nearest neighbor and, probably further. Polymerized fullerenes, rhombohedral and tetragonal, are quasi two-dimensional crystals, and it should be noted that the strong exchange found in our calculations

refers only to the in-plane interaction. We assume the inter-plane exchange interaction J' to be ferromagnetic and weak, similar to that in the low T_C C₆₀-TDAE compounds. Its exact value is not of primary importance, as discussed below.

In our model, a ferromagnetic transition occurs in a solid solution C₆₀R_x where the impurity (dopants) concentration x is small. For small x , the spatial distribution of the dopant is random so that the sites of the fullerene matrix become spin active in a random fashion. Consequently, doped polymerized fullerenes are expected to belong to the class of disordered ferromagnets. Properties of a disordered magnet are commonly discussed in the framework of percolation theory (see Ref. 46 and references therein). A detailed analysis is beyond the scope of the paper, and we limit ourselves to few remarks.

At zero temperature, any two spins are aligned if they are within the range of the exchange interaction. The long-range magnetic order, when the aligned spins belong to the infinite cluster, is established provided the spin concentration, that is the impurity radical concentration, exceeds the percolation threshold. For a two-dimensional square lattice with *only* the nearest neighbors interaction, the critical concentration x_c is $x_c \sim 0.59$. If the interaction extends beyond the nearest neighbors, the critical concentration scales as \mathcal{R}^{-2} with the radius of the exchange interaction \mathcal{R} (measured in units of the lattice constant). Our calculations show that the interaction is not limited to the nearest neighbors, and \mathcal{R} is not less than $2\sqrt{2}$ and then $x_c < 0.07$. In accordance with this estimate, a single impurity radical for 14, or perhaps more, C₆₀ molecules suffices to transform a diamagnetic polymerized fullerene into a ferromagnet.

The assumption of the percolation theory about a random distribution of impurities may be invalid for certain synthesis conditions, when segregation of defects may occur. In this case, the formation of ferromagnetic islands is expected, with or without bulk magnetic order.

Evaluation of the Curie temperature, T_C , is hindered by the presence of disorder and the quasi two-dimensional nature of the polymerized fullerenes. In accordance with the Mermin-Wagner theorem,⁴⁷ two-dimensional (2D) isotropic magnets exhibit a long-range order only at $T=0$ K for any value of the in-plane exchange integral J . In quasi-two-dimensional layered compounds, the magnetic order establishes at a finite temperature T_C due to the inter-plane exchange J' . It is well known⁴⁸ that in the limit of small J' , the Curie temperature can be estimated as $T_C \sim J/\ln(J/J')$; the estimate should be valid for our case of a disordered system unless it is very close to the percolation threshold. In accordance with our *ab initio* calculations, the in-plane exchange interaction is in the range $J=0.1-0.3$ eV=1200–3500 K. Seeing that the dependence of T_C on J' is only logarithmic, the Curie temperature T_C is several times (but not several orders) less than J , i.e., in the range 300–1000 K.

These estimates, although crude, show that the model has the potential to give the interpretation to the experiments⁴⁻¹⁰ where magnetism of polymerized fullerenes was observed at room temperatures and above. These calculation show also that a low magnetization, which is controlled in our model by the concentration of the radicals, is compatible with a high Curie temperature.

The presence of any radicals in the studied samples of polymerized fullerenes is an open question. The only exception is hydrogen, which was detected in a rather large amount (one hydrogen atom per six fullerenes) in some polymerized fullerenes exhibiting high-temperature ferromagnetism.²⁴ Some caution is needed at this point. Hydrogen is known to have the tendency toward the formation of the radical adducts C₆₀H_n with even number n . Our calculations show that the ground state of C₆₀H_n complex is spin singlet for $n=2$, and most likely this conclusion holds for higher even n 's. For this reason, the presence of hydrogen in large amounts does not guarantee magnetism. However, if we are concerned with a *dilute* solid solution of hydrogen, where rare hydrogen atoms are dispersed chaotically in the fullerene matrix, the formation of C₆₀H complexes becomes feasible during the high-temperature synthesis. Formally a metastable state, the system of the C₆₀H complexes quenched upon cooling, is practically stable, being separated from the true energy minimum by a high energy barrier (of the order of 2 eV per pair of hydrogen atoms in accordance with our numerical calculations). In our scenario, the quenched network of the magnetically active C₆₀H sites becomes ferromagnetic below T_C . The formation of the network is obviously sensitive to details of the synthesis conditions, and from this point of view, a poor reproducibility of the magnetic fullerene synthesis procedure can be understood.

Besides hydrogen, the presence of fluorine, hydroxyl group OH, amino group NH₂, and methyl group CH₃, is favorable, in accordance with our *ab initio* calculation, for the high-temperature ferromagnetic phase of polymerized fullerenes. Since these materials have not yet been synthesized and measured, this is a theoretical possibility waiting for experimental verification.

As has been already mentioned, a similar mechanism of ferromagnetism is responsible for a low temperature transition of the C₆₀ fullerene intercalated with the donor TDAE molecules. The exchange interaction is much weaker in this case³ because the mutual orientation of the adjacent fullerenes differs from that in the polymeric phases.

In conclusion, we have considered a mechanism of ferromagnetism in polymerized fullerenes, where diamagnetic C₆₀ molecules transform into stable paramagnetic species, ions C₆₀[±] or fullerene radical adducts C₆₀R, and become magnetically active due to the charge and spin transfer from radical impurities. The model is supported by *ab initio* calculations, the main result of which is that in the [2+2] cycloadduct polymerized phase the effective exchange interaction between the paramagnetic species is ferromagnetic and strong enough to account for the high-temperature ferromagnetism observed in recent experiments on polymerized fullerenes. The model predicts ferromagnetism with the high Curie temperature in the polymerized fullerenes doped with the radicals like hydrogen, fluorine, hydroxyl group, amino group, or methyl group.

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