

Magnetic ordering in C₆₀ polymers with partially broken intermolecular bondsV. V. Belavin,¹ L. G. Bulusheva,¹ A. V. Okotrub,¹ and T. L. Makarova²¹*Nikolaev Institute of Inorganic Chemistry SB RAS, Prospekt Ak. Lavrenteva 3, 630090, Novosibirsk, Russia*²*Department of Physics, Umea University, S-90187 Umea, Sweden*

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The possibility of formation of radical centers in a hexagonal C₆₀ polymeric layer, without damage to the fullerene cages, is shown. The geometry optimization of C₆₀ trimers and tetramers using the semiempirical AM1 method has revealed that linking of molecules through a single bond is preferred for multiplet states of system. The density of unpaired electrons is mainly localized in the vicinity of the single bonds producing narrow energy bands near the Fermi level of hexagonal C₆₀ polymers. The magnetic state of the polymer depends on the number and location of single bonds in a polymeric layer.

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I. INTRODUCTION

Ferromagnetic behavior of the rhombohedral C₆₀ polymer¹ was one of the unexpected discoveries in the field of research of fullerenes under high pressure. The samples, synthesized at temperatures and pressures close to the conditions of C₆₀ collapse, showed a history dependent magnetic behavior (hysteresis) up to 500 K. The magnetic carbon samples were prepared at three pressures: 2.5,² 6,^{1,3} and 9 GPa⁴ at temperatures approximately 100 K lower than that which causes C₆₀ cage damage. It had been assumed that magnetic ordering in the rhombohedral polymer is caused by the defects developed in the polymeric network under extreme synthetic conditions. Transmission electron microscopy shows that the radical centers are formed in the polymeric state before collapse, without damage to the fullerene cages.⁴ This is confirmed by the Raman and x-ray measurements.²

For the explanation of the origin of magnetism, various models have been offered. Thus it was shown⁵ that occurrence of atomic vacancies in C₆₀ molecules comprising the hexagonal polymerized layer results in the appearance of localized electronic spins. Carbon radicals could be introduced by negative Gaussian curvature⁶ arising from fullerene coalescence. The Stone–Wales transformations of C₆₀ molecules were found to result in opened cage structures acquiring a magnetic moment of several Bohr magnetons.⁷ Finally, in Ref. 8, it was shown that the state responsible for the presence of magnetic interactions in the C₆₀ dimer is the triplet state obtained when one of the two interfragment C–C bonds is broken under the influence of applied pressure. Moreover, total energy calculations have shown that the triplet state of the species remains magnetically active after load removal.⁸

Based on the experimental data^{1–4} and in opposition to the previous models^{5–7} we propose an alternative mechanism of formation of radical centers in C₆₀ polymers where the appearance of magnetic moments is due to a partial breaking of intermolecular bonds. We propose that this kind of structural modification is the most plausible under the synthesis conditions used, and our arguments are the following. The angles in four-membered rings bridging the molecules in the polymer are equal to 90°,⁹ i.e., far from the tetrahedral value characteristic of sp³-hybridized carbon. The resulting struc-

tural strain should considerably reduce the dissociation energy of the intermolecular bond compared with that of the intramolecular one, thus we believe that the defects appearing in the polymerized C₆₀ layers under the extreme synthesis conditions are neither vacancies nor coalescence, but rather broken interfullerene bonds.

The purpose of the present work is the quantum-chemical modeling of the structures of polymerized C₆₀, which give the origin of spin moments and the conditions for their ordering. We have constructed several models representing molecular clusters of polymerized C₆₀, in which some of the molecules are linked through a single bond (one intermolecular C–C bond). Thus we have modeled an effect of high temperature of synthesis. The geometry of model structures was optimized in singlet and multiplet states to find the conditions that stabilize single bond formation.

II. DETAILS OF CALCULATIONS

We took one trimer and two tetramer structures (Fig. 1) comprising covalently bonded C₆₀ molecules, where we broke one or two of the interfullerene bonds in the four membered rings arising from [2+2] cycloaddition. In the initial structures, the distance between atoms A' and B', C' and D', previously participating in the formation of intermolecular bonds, was taken as 2.4 Å: this spacing prevents covalent bonding. The breakage of one of the two intermolecular bonds in structure I gives rise to two unpaired electrons. Antiparallel and parallel alignment of the electron spins results in the singlet and triplet states of the system, respectively. For the structures II and III, the spin state arises from the spin of the four localized electrons. These four spins can be coupled either as singlet, triplet, or quintet states. The geometry of the molecular clusters so constructed was optimized with the unrestricted Hartree-Fock self-consistent field method using semiempirical AM1 parametrization¹⁰ within the GAMESS package.¹¹ The geometry was relaxed without any symmetry constraints to the gradient value of 10⁻⁴ Ha/Bohr.

The optimized geometry of clusters was then used for the construction of hexagonal layers of polymerized C₆₀ and the calculation of band electronic structure of polymeric layers

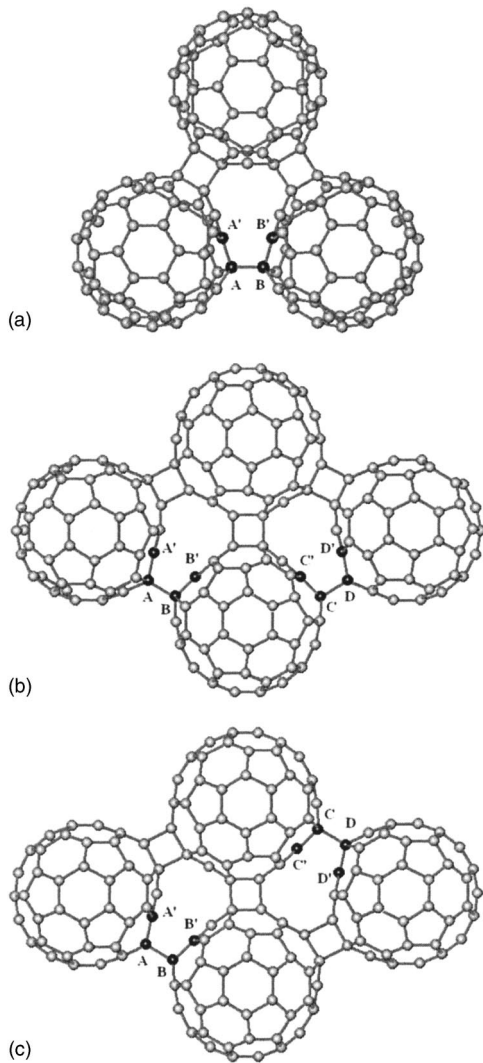


FIG. 1. Molecular clusters of polymerized C_{60} with broken bonds between A' and B' atoms and C' and D' atoms. (a) Trimer C_{60} (structure I) with two singly bonded molecules, (b) tetramer C_{60} (structure II) incorporates three adjacent molecules involved in single bonding, and (c) tetramer C_{60} (structure III) links two pairs of singly bonded molecules.

was carried out using an empirical tight-binding (TB) method¹² with first neighbor interactions. The hopping parameters of the empirical TB Hamiltonian were specially chosen to reproduce the main features of the x-ray emission spectra of fullerenes C_{60} and C_{70} (Ref. 13) and had the

TABLE I. Total energy (in a.u.) of clusters of Fig. 1 optimized by the AM1 method.

	Singlet state	Triplet state	Quintet state
Structure I	-843.68	-843.74	
Structure II	-1124.96	-1125.02	-1125.02
Structure III	-1124.96	-1125.01	-1125.01

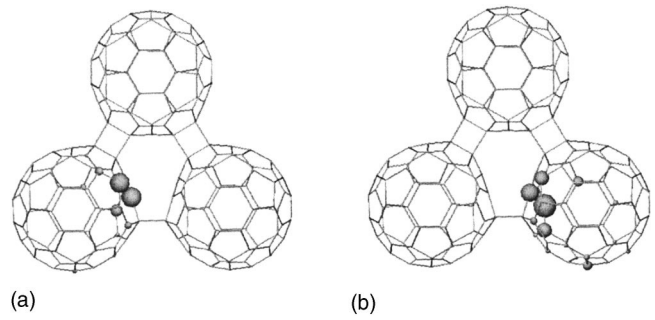


FIG. 2. Schematic representation of electronic density distribution for the two highest occupied molecular orbitals of C_{60} trimer in triplet state.

following values: $E_s = -3.650$ eV, $E_p = -3.650$ eV, $V_{ss\sigma} = -3.630$ eV, $V_{sp\sigma} = -4.5$ eV, $V_{pp\sigma} = -5.38$ eV, and $V_{pp\pi} = -3.04$ eV. This set of hopping parameters provides correct π -electronic density distribution in the valence bands of fullerenes and energy separation of π - and σ -electronic sub-systems.

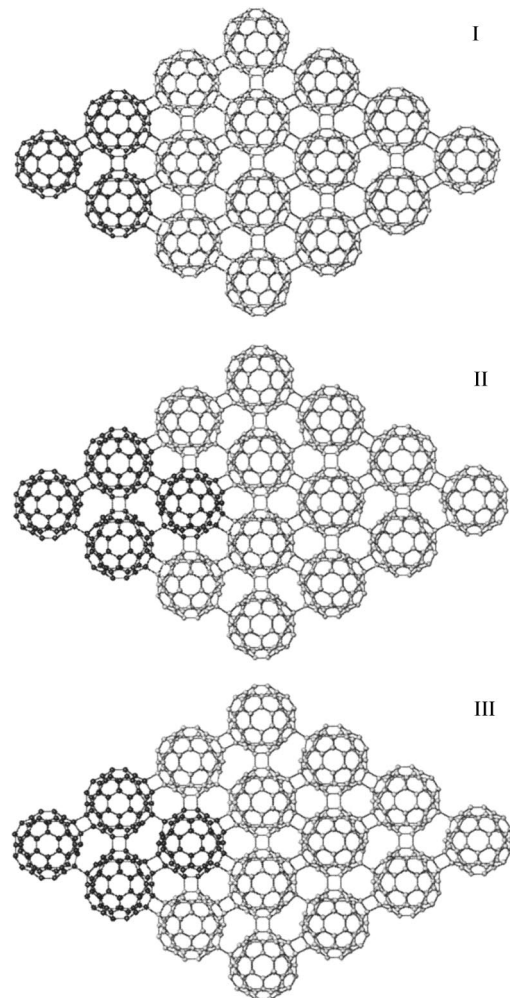


FIG. 3. Fragments of hexagonal polymerized C_{60} layers I-III. Unit cells are highlighted.

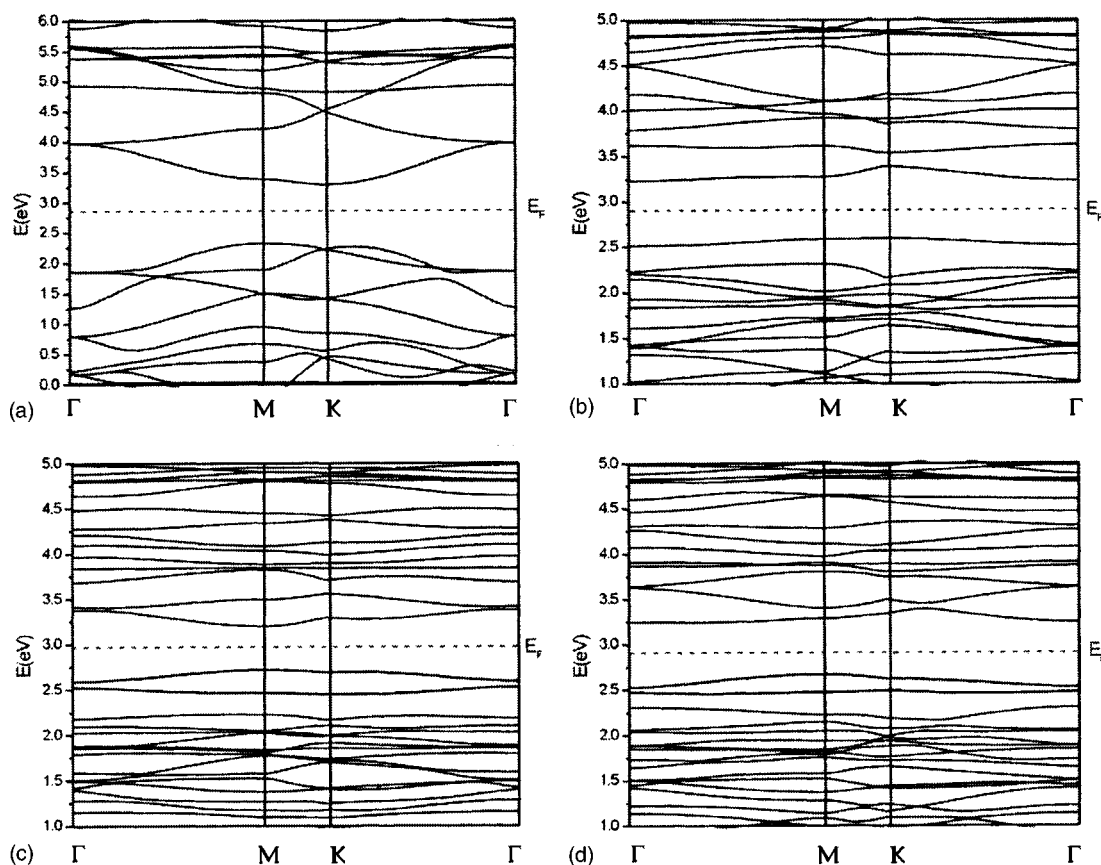


FIG. 4. Band structure of polymerized C₆₀ layers: (a) hexagonal layer with standard intermolecular bonding; (b)–(d) model layers I, II, and III, respectively. The flattened upper occupied bands in the electronic structure of layers I–III are highlighted.

III. RESULTS AND DISCUSSIONS

A. Electronic structure of clusters

The geometry optimization of structures I–III in singlet state resulted in reformation of the four-membered rings between molecules. Antiparallel alignment of unpaired electrons allows overlapping of electron clouds to produce a covalent bond between atoms A' and B', C' and D'. Thus linking of C₆₀ molecules through a single bond is unfavorable for a system in singlet state in agreement with other previous theoretical studies.^{14,15} However, for multiplet states of structures I–III the single bonds are preserved. The optimized length of the single bond AB (CD) is equal to 1.55 Å, i.e., close to the distance in diamond. Comparison of total energies of clusters (Table I) demonstrates the energetic stability of high spin states. The different arrangement of single bonds in structures II and III has practically no effect on the energy of the system. Moreover, the results of calculation point to the absence of a barrier for the transition of C₆₀ tetramers from the triplet state to the quintet one.

To answer the question what kind of interactions result in stabilizing of structures with a single bond and in the triplet state, we have considered the changes in the electronic structure of a trimer (structure I) with transition from the standard [2+2] cycloaddition to a single intermolecular bond. The molecular orbitals (MOs) responsible for the intermolecular σ -bonding between fullerenes are situated approximately

9 eV below the highest occupied MO (HOMO) of the polymeric structure. The formation of a single intermolecular bond results in a slight increase in energy of these orbitals, while the π -electrons of atoms A' and B' occupy the upper levels. Figure 2 schematically shows the electron density distribution for the two upper levels of the C₆₀ trimer in the triplet state. Electronic density attributed to these MOs is mainly distributed over the C₆₀ cage, including the single intermolecular bond, and has a tendency to localize at and around the atoms with dangling bonds. Spin alignment in the triplet state of the C₆₀ trimer causes repulsion between the unpaired electrons of atoms A' and B' and stabilizing single bonding. The optimized distance for the A'B' pair is 2.39 Å, close to the spacing in the initial configuration of the trimer.

The analysis of the electronic structure of C₆₀ tetramers possessing two single bonds [Figs. 1(b) and 1(c)] has shown that in the triplet state the electron spins are aligned for atoms A' and B' but antialigned for the C'D' pair. The antialignment causes a reduction of the distance between atoms C' and D' down to 2.31 Å, which is, however, still far from the value for the covalent bond. Steric limitation in the tetramer network probably stops the atoms approaching. The geometry optimization of structures II and III in the quintet state gives the same spacing (2.39 Å) between atoms C' and D' and A' and B'. The distance between the centers of adjacent C₆₀ molecules in the considered structures varies from 9.13 to 9.40 Å and has a maximal value when the molecules are singly bonded.

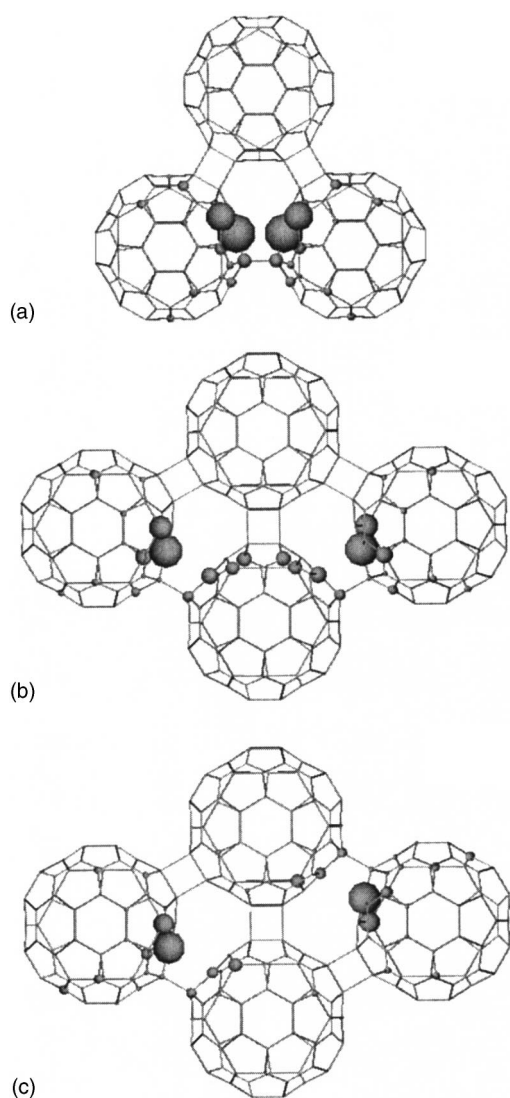


FIG. 5. Schematic representation of the upper occupied crystal orbital in the center of Brillouin zone of layer I (a), layer II (b), and layer (c). Fragments corresponding to the unit cells of polymerized layers are shown.

Quantum-chemical calculations predict localization of radicals in carbon caged systems with the development of defects, for example, vacancies in C_{60} (Refs. 5 and 7) or negative curvature of graphitic surface.⁶ We have proposed a way for electron spins localization in the polymerized C_{60} systems without any structural change of fullerene molecules. Carbon radicals are stabilized by the specific geometry of the atom which was previously involved in the interfullerene bond. The distance between this trivalent atom and its neighbors exceeds 1.43 \AA that, being larger than the “double” fullerene bond, considerably reduces the efficiency of π -electron overlap. The spin density per C_{60} was estimated by summing spin populations of atoms composing a fullerene molecule. The value obtained is equal to 0.5 for singly bonded C_{60} and close to zero for cages with standard intermolecular bonds. It supports the localization of unpaired electrons.

B. Electronic structure of polymerized layers

Some insight into the properties of the material can be obtained by comparing electrical and magnetic properties of polymerized fullerenes. Conductivity of ferromagnetic samples was shown to be intermediate between the semiconducting behavior of the usual rhombohedral polymerized phase and the metallic behavior of the postfullerene phase where C_{60} cages are almost completely destroyed.^{2,16} To reveal characteristic features of the electronic structure of C_{60} polymers possessing single intermolecular bonds we calculated the hexagonal layer with the standard interfullerene bonds and hexagonal layers constructed from the molecular C_{60} clusters considered above. The fragments of model layers are shown in Fig. 3. The models differ in proportion and location of single bonds. The unit cell of layer I consists of three molecules, two of them linked through a single bond. The unit cells of layers II and III contain four molecules. Three adjacent molecules in layer II are connected via single bonds; the fourth molecule is linked via four-membered rings. Layer III is constructed from pairs of singly bonded C_{60} . The distance between adjacent molecules in the polymeric layers is 9.1 \AA , i.e., close to the experimentally determined value.⁹

Tight binding calculations of the hexagonal polymerized layer with standard bonding predict a semiconductor band structure with an indirect gap of 0.98 eV [Fig. 4(a)]. This value is significantly larger than the fundamental energy gap of 0.35 eV obtained for the rhombohedral C_{60} polymer within local density approximation (LDA).¹⁷ Taking into account the tendency of the LDA method to underestimate the width of the forbidden gap, we suppose the TB values should be somewhat closer to the experimental ones. In any case these results provide a qualitative picture of changes in the electronic structure of polymerized C_{60} with breaking of a certain proportion of the intermolecular bonds.

Band structures of the polymerized C_{60} layers are compared in Fig. 4. The rupture of the four membered ring, leaving only a single intermolecular bond, results in a decrease in the fundamental energy gap to 0.64 , 0.45 , and 0.57 eV , respectively, for the layers I, II, and III. Furthermore, relative to the polymer with standard bonding, the layers I–III are characterized by lower energy dispersion of the crystal orbitals (COs). Significant narrowing of the upper occupied COs and their separation from other branches of the valence band evoke a special interest. One band with a width of 0.08 eV is situated below the Fermi level in layer I [Fig. 4(b)], while two occupied narrow bands are formed in the electronic structure of the layers II, III [Figs. 4(c) and 4(d)]. Obviously, the number of such bands (or bands of this type) is defined by the number of single bonds in the unit cell of the polymerized layer. Electronic density assigned to the two upper occupied MOs of the C_{60} trimer in the triplet state was found to be localized in the vicinity of the atoms which previously participated in the interfullerene bonding. With this result in view, the narrow upper bands of the polymerized C_{60} layers are occupied by π -electrons originating from dangling intermolecular bonds.

Figure 5 represents a schematic structure of the upper occupied CO of layers I–III in the center of the Brillouin

zone. The C₆₀ cages constituting the unit cell of the layer are shown. For each atom the size of the sphere is proportional to the value of valence electron density. Electrons from the upper CO of layer I are mainly distributed over singly bonded cages with the greatest localization around the atoms with broken intermolecular bonds [Fig. 5(a)]. The double level occupancy results in identical electron density for both C₆₀ cages. A similar picture is characteristic of the upper CO structure of layers II and III [Figs. 5(b) and 5(c)]. Predominant electron accumulation on atoms A' and D' (see atom notation in Fig. 1) is due to the occurrence of two single bonds in the unit cells of the polymers. The second narrow CO gives localization of electron density mainly at the atoms B' and C' belonging to adjacent fullerenes. We believe that the localized electrons are responsible for the ferromagnetic ordering in the C₆₀ polymers. The large spacing of electron spins in the models considered here considerably diminishes the efficiency of direct exchange. An indirect exchange coupling requires a special medium providing the correlation between spin moments. The unpaired electrons are part of the π -system of the C₆₀ cage which, due to its high polarizability, could flip a close neighboring spin. The ability of C₆₀ to act as a magnetic coupling unit between radical centers has been evaluated,¹⁸ and the C₆₀ diradical was shown to be a magnetic coupler, whose ferro- or antiferromagnetic behavior can be tailored depending on the relative position in which the radical centers are attached to the C₆₀ diradical.

IV. CONCLUSION

The unusual magnetic properties of the rhombohedral phase of polymerized C₆₀ were detected for the samples synthesized at conditions close to the stability limit of the polymer. The further enhancement of pressure and temperature results in the collapse of C₆₀ cages. We suggest the partial disruption of interfullerene bonds is responsible for radical center formation. The C₆₀ molecules in a hexagonal layer are normally linked through a four-membered ring. The high temperatures of synthesis can result in the breaking of one side of the ring between molecules that produces two unpaired electrons on the adjacent molecules. This process will most likely have a random character and the fast quenching of the sample should preserve the metastable state of the polymer. Spin flip of an unpaired electron creates a local magnetic moment that stabilizes the single interfullerene bonds. The number and arrangement of single bonds in a polymerized layer can have a strong impact on the energy gap and magnetic moment of the sample. We have revealed a tendency for the energy gap to decrease in hexagonal layers with increasing of numbers of single intermolecular bonds. Furthermore, we propose that, under extreme synthetic conditions, some of the molecules comprising the hexagonal layer can transform into structures with single intermolecular bonds. Such a transformation can be responsible not only for the magnetic properties of the sample, as we have shown for certain fragments, but also for electrical properties.

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