«Scaly» magnetism of carpet-like polymers of C60

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Since its discovery, high-temperature magnetism of carbon crystals, formed by polymerized layers of covalently bound C_{60} molecules, still has been an intriguing phenomenon of obscure origin. The paper is devoted to disclosing the problem by quantum-chemical calculations of large clusters of both hexagonally and tetragonally packed carpet-like C_{60} layers. The calculations have been performed in the UHF SCF HF approximation by using AM1 semi empirical technique of the NANOPACK parallel codes [1]. Exchange integrals J are considered as the main characteristics of magnetic phenomena. They are determined as

$$J = \frac{E_{S=0}^{UHF} - E_{S_{max}}^{UHF}}{S_{max}^2}, \quad where \quad E_{S=0}^{UHF} \quad and \quad E_{S_{max}}^{UHF}$$

are the cluster energies in the spin-mixed singlet state as well as in the state with the highest multiplicity *2Smax+1* related to spin *Smax=n/2*. The number of non-paired odd electrons *n* for a cluster with *k* polymerized C_{60} molecules fills in the region of $60\kappa \div 52\kappa$ and $60\kappa \div 48\kappa$ for tetragonal and hexagonal structures, respectively.

Clusters considered in the paper cover k varying from 2 to 10. As shown, exchange integrals J_{mol} related to one C_{60} molecule slightly decreases with respect to a free molecule while k is growing but still remains negative and too large by value to provide magnetic behavior. Therefore, the molecules themselves can not provide magnetism of ideal crystals consisted of polymerized molecules. However, the exchange integral of a cluster of k C60 molecules as a whole is determined as $J_{cl} \sim J_{mol}/\kappa$ [2] so that at big k it may approach value to be enough for magnetic behavior observation. This conclusion is well consistent with a recent experimental finding of a direct connection between magnetic behavior of polymerized carbon crystals and well observed domain structure of the latter [3].

1.   P.K.Berzigiyarov, V.A.Zayets, I.Ya.Ginzburg, V.F.Razumov, E.F.Sheka Int.Journ.Quant.Chem., 88 (2002) 449.
2.   L.Noodleman. J.Chem.Phys. 74 (1981) 5737.
3.   K.-H. Han et al. Carbon 2003 (in print).

Two building stones of atomic-level magnetism:

1. Unpaired electrons
2. Structure

1.Unpaired electrons

1. No experimental evidences
2. Theoretical concepts:
   2.1. C_{60} molecule has no unpaired electrons and ideal crystals of
       polimerized C_{60} are non-magnetic:
       S.Okada et. al, Phys.Rev. 1995, 1997, 2003;
   2.2. Unpaired electrons appear as radicals due to
       * structure defects
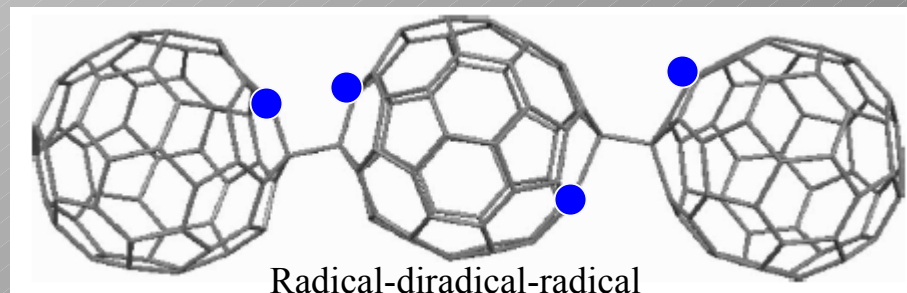   *A.N.Adriotis et al. Phys.Rev.Letts. 2003;*
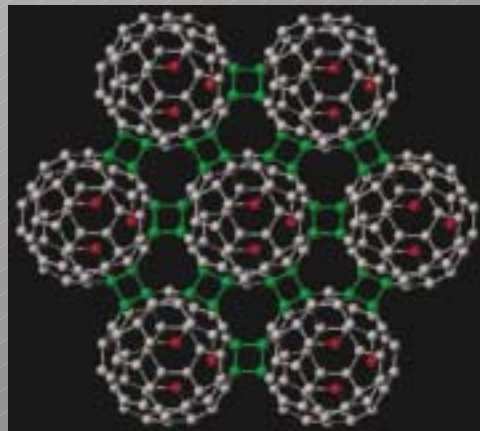
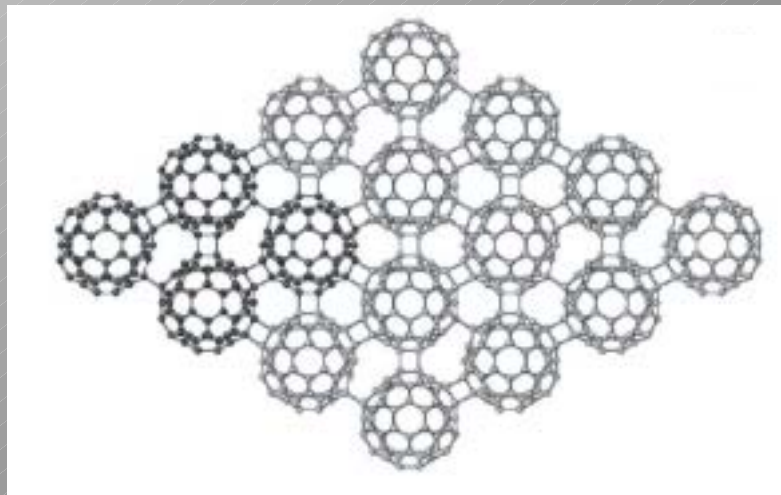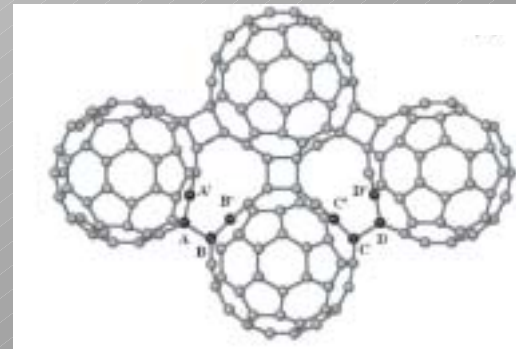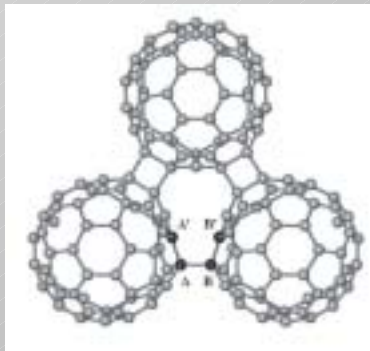* topological defects
  N.Park et al. Phys.Rev.Letts. 2003;
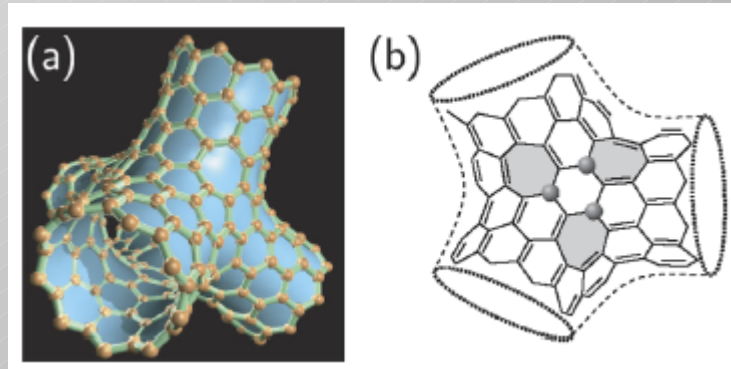
* defects caused by photoexcitation
  J.Ribas-Arino, J.J.Novoa J.Phys.Chem.Solids 2004.

Radical-diradical-radical

* magnetic ordering in C_{60} polymers with partially broken intermolecular bonds

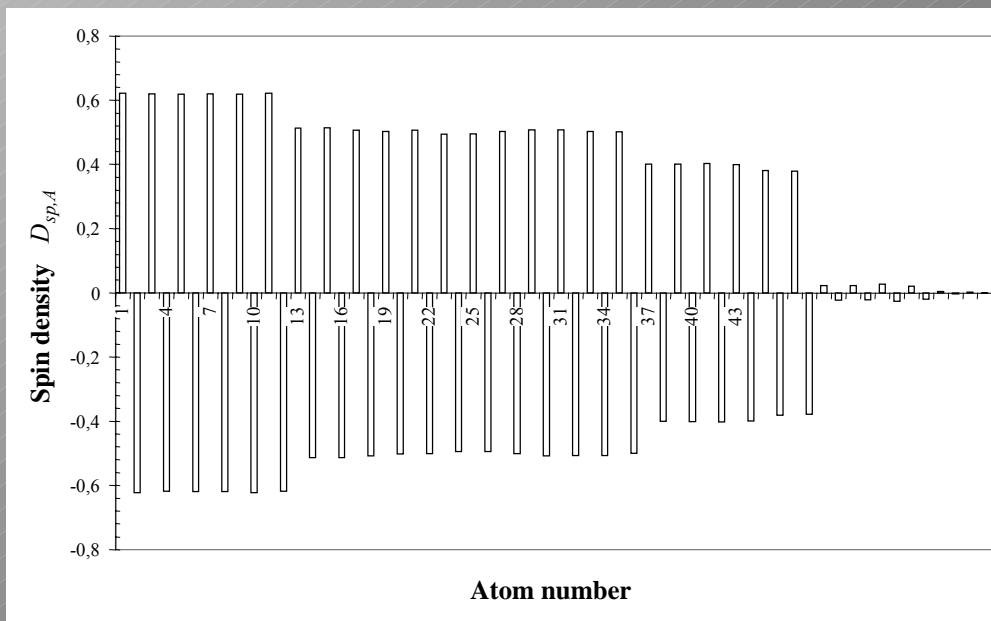*V.V. Belavin1, L.G. Bulusheva1, A.V. Okotrub1, T.L. Makarova*

The main idea of the current study:

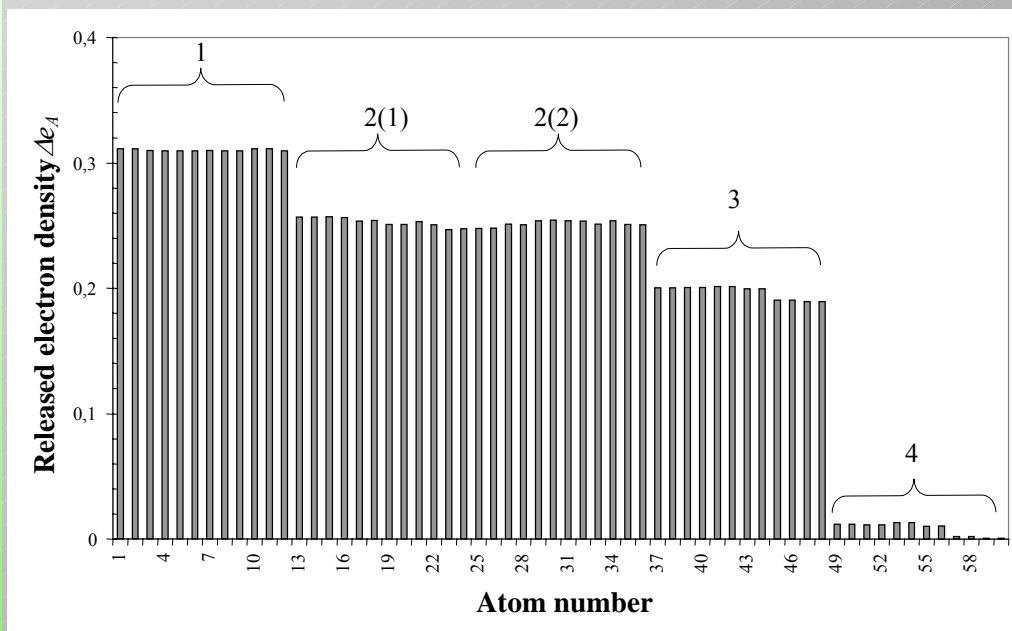# Molecule C_{60} itself
is the source of unpaired electrons

Spin density distribution over
C_{60} molecule atoms in the
singlet state:
UHF HF calculations

$$D_{sp,A} = \sum_{i \in A} P_{ii}^{\alpha} - P_{ii}^{\beta}$$

Released electron density (RED) distribution over
C_{60} molecule atoms in the singlet state:
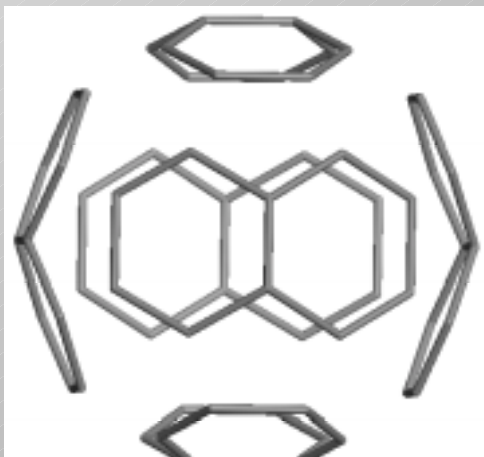UHF HF calculations

$$\Delta e_A = 0.5 * \left| D_{sp,A} \right|$$
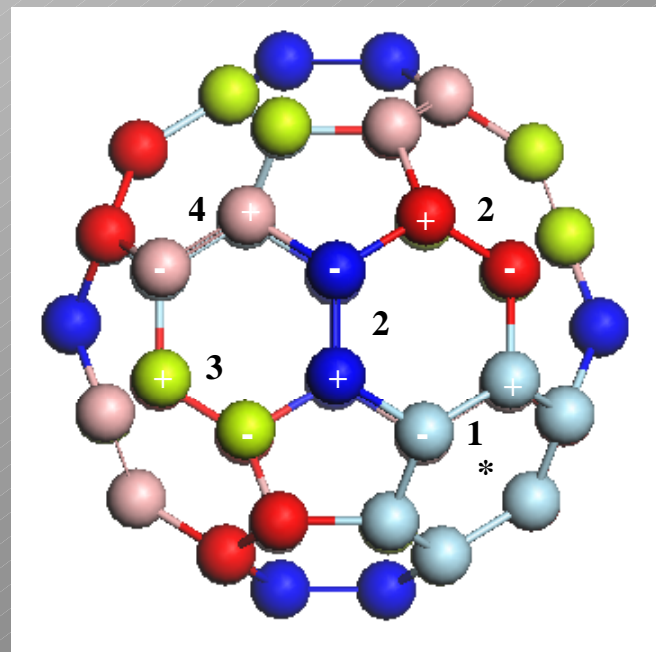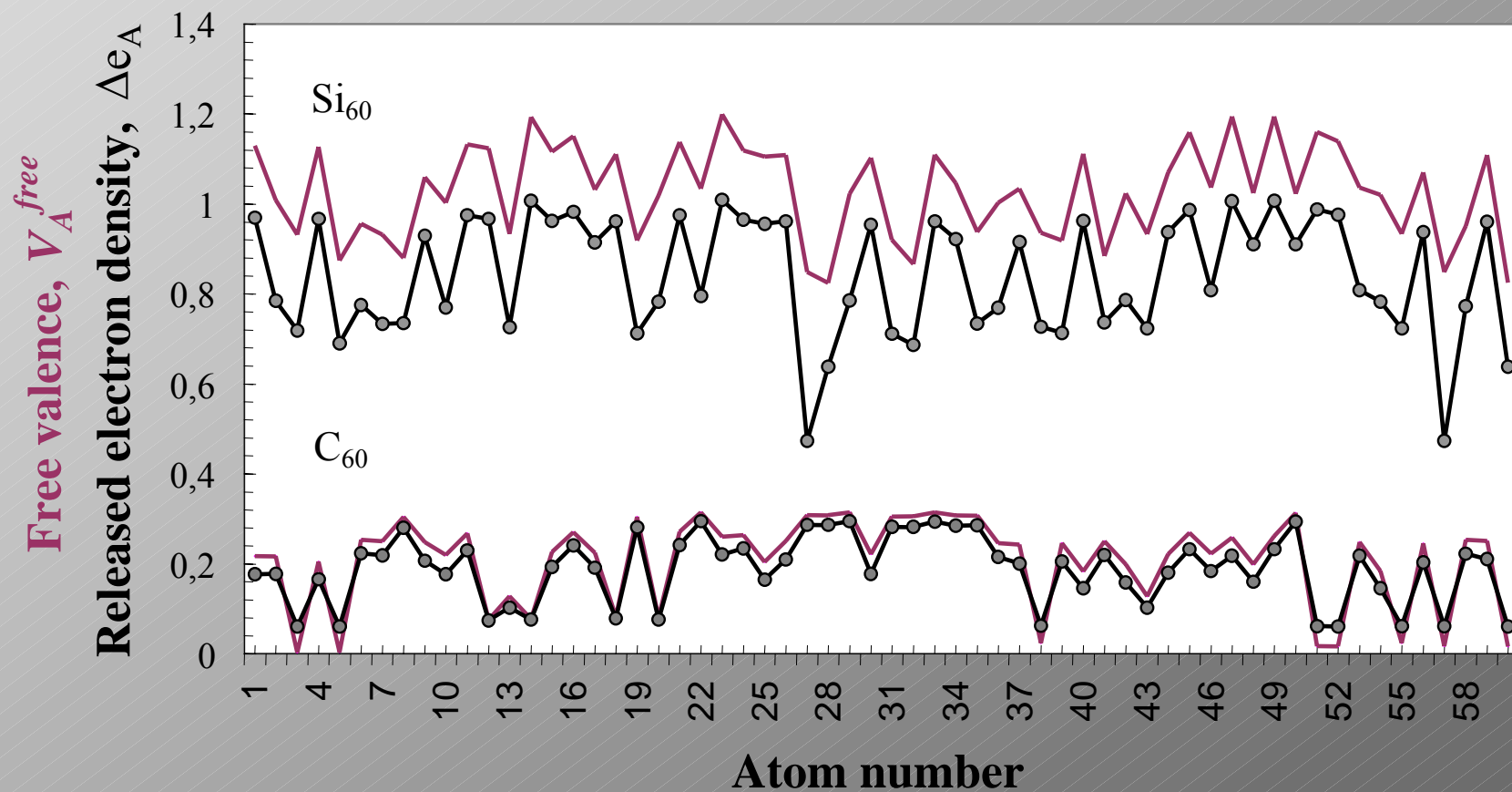
Sheka, 2004

Spin-portrait of the C_{60} molecule
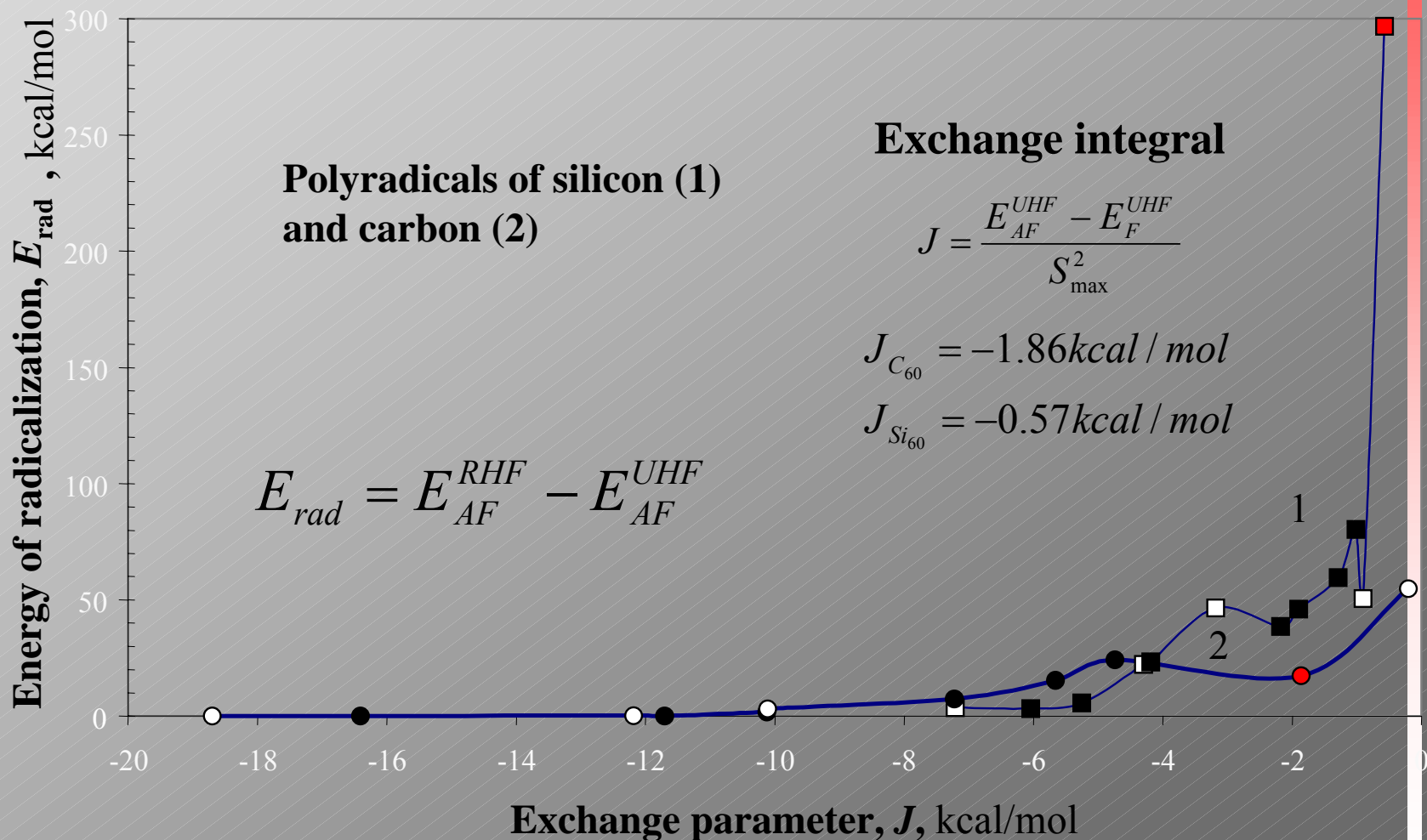

6* C_{10} model
Bulychev@Udod, 1995

Sheka, 2004

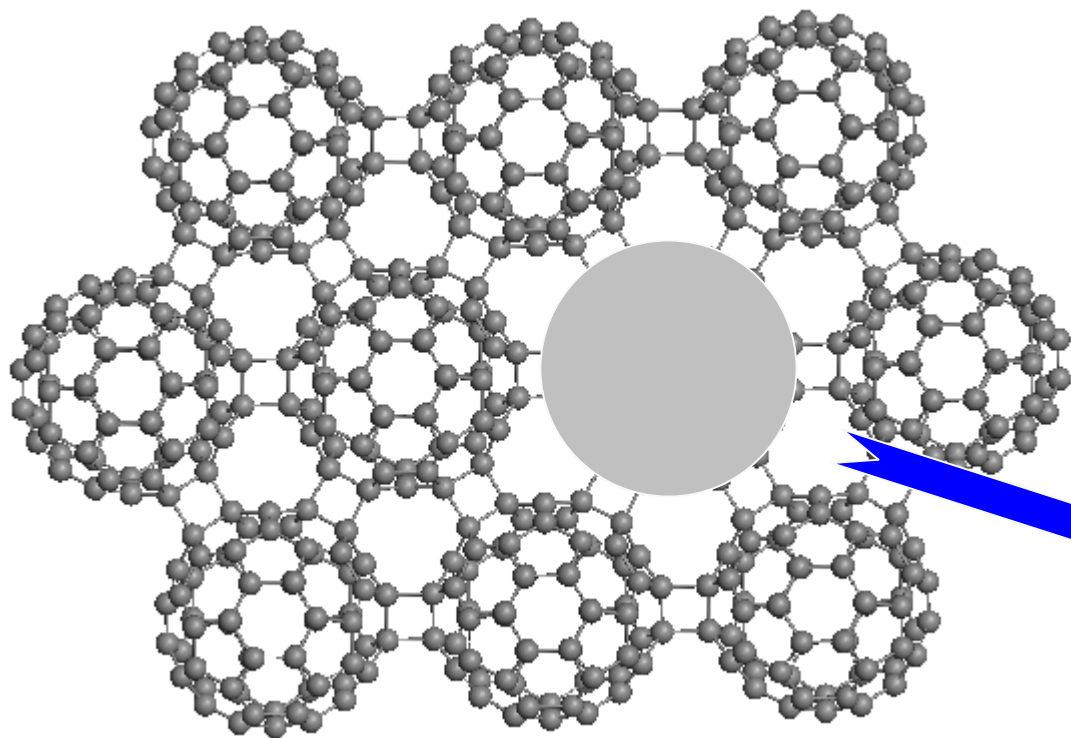# Are unpaired electrons of the C_{60} molecule magnetic?

Free valence, V_A^{free}

Released electron density, Δe_A

Si_{60}

C_{60}

Atom number

$$V_A^{free} = N_A^{val} - \sum_{B \neq A} K_{AB}$$

Answer: No, due to a large value of exchange integral

Energy of radicalization, E_{rad}, kcal/mol

Polyradicals of silicon (1) and carbon (2)

Exchange integral

$$J = \frac{E_{AF}^{UHF} - E_{F}^{UHF}}{S_{max}^2}$$

$$J_{C_{60}} = -1.86 \, kcal/mol$$

$$J_{Si_{60}} = -0.57 \, kcal/mol$$

$$E_{rad} = E_{AF}^{RHF} - E_{AF}^{UHF}$$

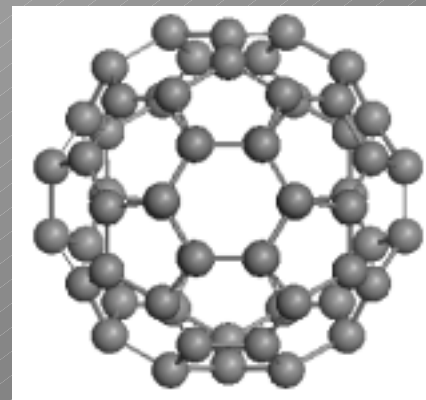Exchange parameter, J, kcal/mol

What is going with unpaired electrons of the C_{60} molecule under polymerization?

Rhombohedral modification

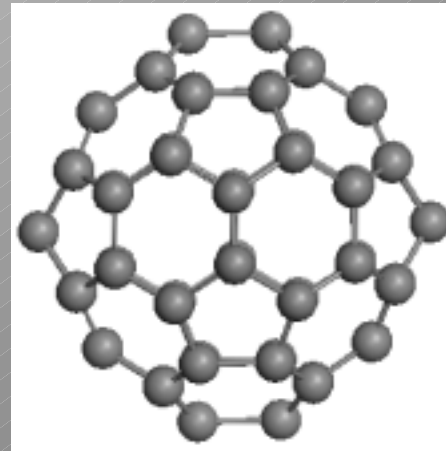The main element of the crystal unit cell (rhombohedral modification)

Exchange integral increases under polymerization

$$J_{C_{60}} = -2.07 \, kcal/mol$$

What is going with unpaired electrons of the C_{60} molecule under polymerization?

Tetragonal modification

The main element of the crystal unit cell (tetragonal modification)

Exchange integral increases under polymerization

$$J_{C_{60}} = -2.09 \, kcal/mol$$

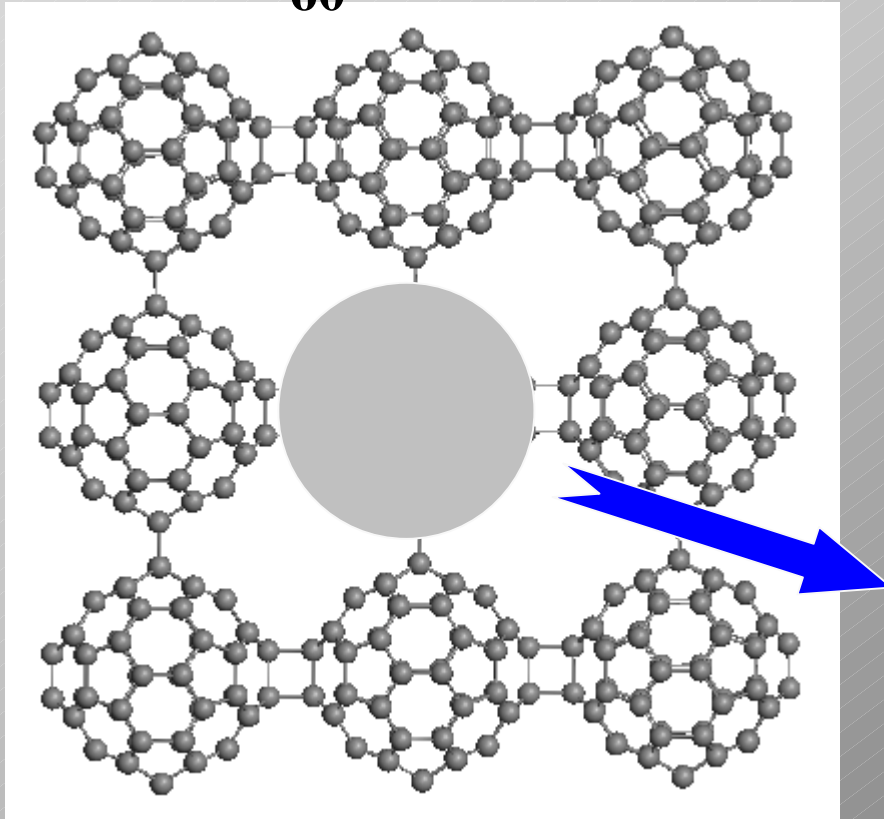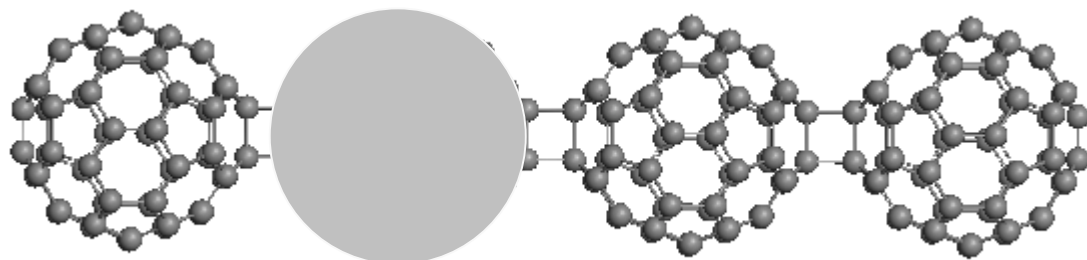# What is going with unpaired electrons of the C_{60} molecule under polymerization?

Orthorhombic modification

The main element of the crystal unit cell (orthorhombic modification)
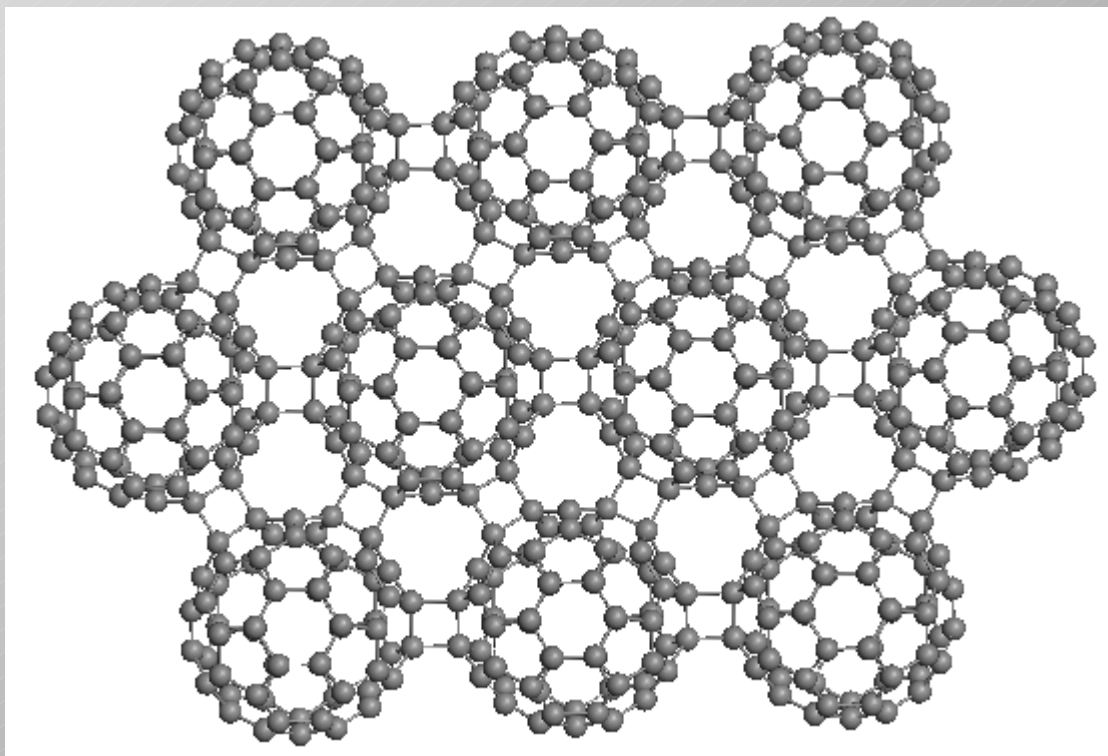
Exchange integral increases under polymerization

$$J_{C_{60}} = -2.07 kcal / mol$$

Conclusion 1: A large value of exchange integral related to unpaired electrons of the C_{60} molecule prevents from magnetic behavior of C_{60} -polymerized crystals of any modification

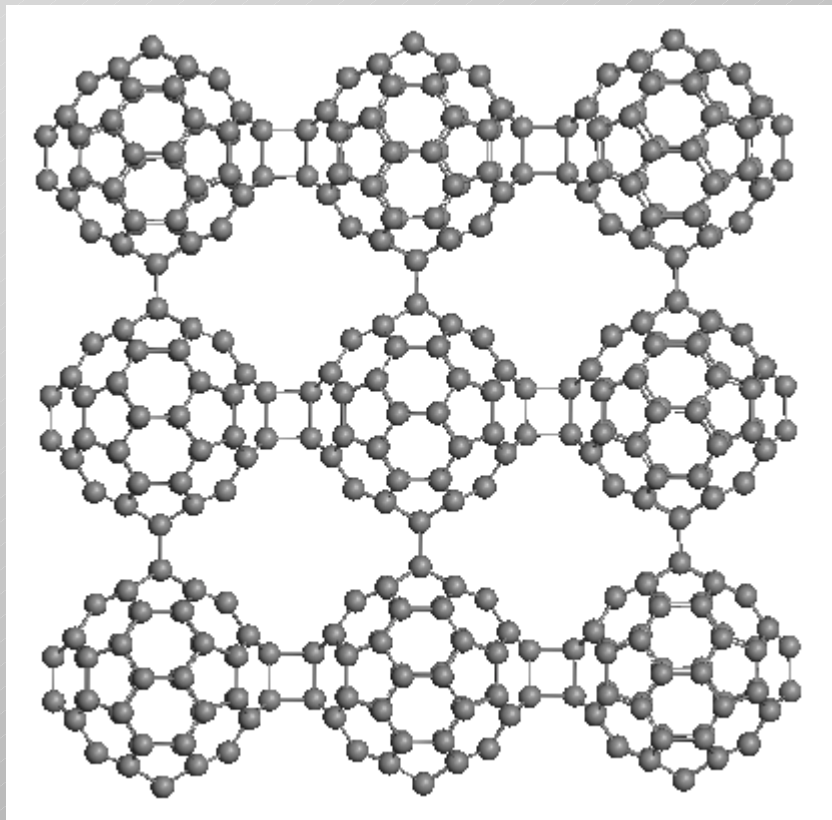# «Scaly» magnetism of polymerized C_{60}

Rhombohedral modification

$$J_{nC_{60}} \sim 1/nJ_{C_{60}}$$

$$J_{nC_{60}} = -0.34 \, kcal/mol$$

Exchange integral substantially decreases when C_{60} molecules are joined in a size-limited polymer
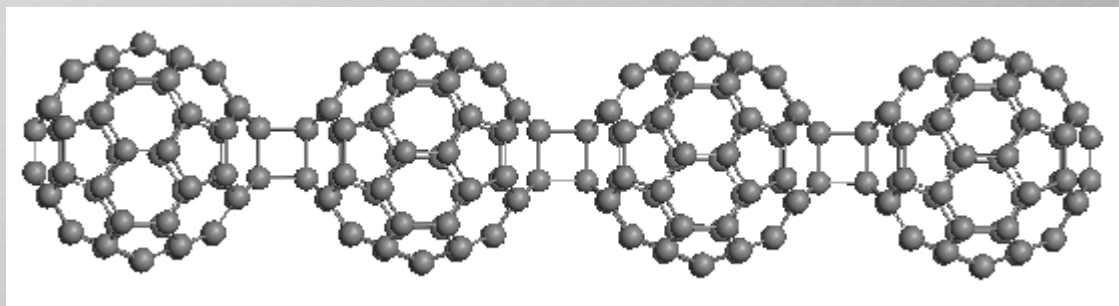
«Scaly» magnetism of polymerized C$_{60}$

Tetragonal modification

$$J_{nC_{60}} \sim 1/nJ_{C_{60}}$$

$$J_{nC_{60}} = -0.38 kcal/mol$$

Exchange integral substantially decreases when C$_{60}$ molecules are joined in a size-limited polymer

«Scaly» magnetism of polymerized C_{60}

$$J_{nC_{60}} \sim 1/nJ_{C_{60}}$$

$$J_{nC_{60}} = -0.72 kcal/mol$$

Exchange integral substantially decreases when C_{60} molecules are joined in a size-limited polymer

Conclusion 2: Magnetism should be expected in nanostructured materials based on a continuous network of C_{60} molecules

Conclusion 3: Magnetism in nanostructured materials is provided by weakening interaction between intrinsic unpaired electrons

Building stones of atomic-level magnetism: 2. Structure: experimental evidence

1. **Magnetism is characteristic only for pressure-polymerized rhombohedral modification** (*Makarova, 2001*)

2. **As well as for photopolymerized orthorhombic modification** *(Murakami, 1996; Makarova, 2001; Owens et al. 2004)*

3. **Rh-magnetism is observed for samples which are produced at high temperature close to the limit of crystal destruction** *(Makarova,2001; Wood, 2002)*

4. **Rh-magnetic samples posses high mosaicity** *(Tokumoto, 2000)*
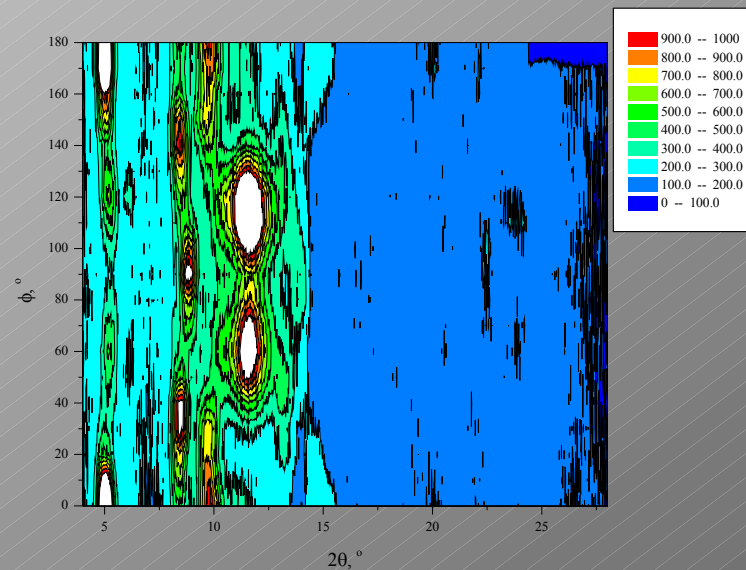
5. **Rh-magnetic sample are characterized by a non-uniform magnetic structure, which constitutes not more than 30% of the sample**

(Han, 2003)
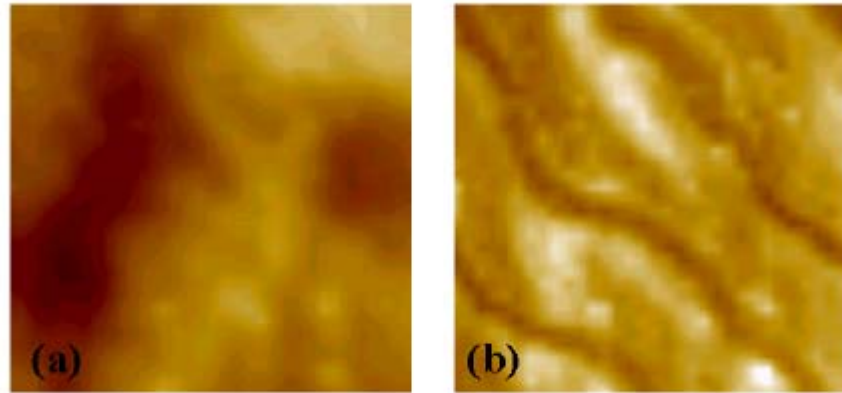
Figure 5. Topographic (a) and magnetic force gradient (b) images taken from the pure region (region A). Here the scan area was 10 μm × 10 μm and scan height 100 nm for MFM image.

6. **Photopolymerized magnets are composed of oligomers with up to ~20 monomers**

(Owens, 2004)

7. **Tetragonal sample do not exhibit either nanostructuring or magnetism at any technique of preparation**

(Makarova, 2001; Davydov, 1999)

Other nanostructured carbon materials showing magnetic behavior

1. **Carbon nanograins in zeolit Y, the magnetic behavior is similar to that for rh_C$_{60}$ magnets**

   (Kopelevich, 2003)

2. **cluster-assembled carbon nanofoam**

   (Rode, 2002)

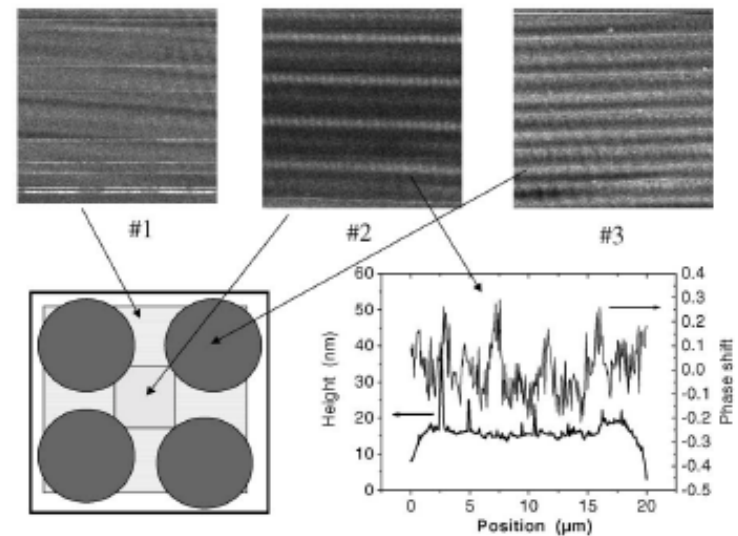3. **Proton-bombarded graphite**

   (Esquinazi)

FIG. 3. Top: Phase gradient pictures obtained at room temperature from MFM at three surfaces of sample 1 corresponding to the irradiation stages No. 1, No. 2, and No. 3; see sketch at the bottom left of the figure. Bottom right: Topography and phase gradient line scans of the middle MFM picture obtained at stage No. 2.

Carbon magnetism is not atomic by origin but is a result of nanostructuring of carbon materials with potentially unpaired electrons