

# To the problem of the intrinsic magnetism in carbon-based systems: pro et contra<sup>1</sup>

A. L. Kuzemsky

*Bogoliubov Laboratory of Theoretical Physics,  
Joint Institute for Nuclear Research, Dubna, Russia.  
kuzemsky@theor.jinr.ru; http://theor.jinr.ru/~kuzemsky*

## Abstract

The arguments supporting the existence of the intrinsic magnetism in carbon-based materials including pure graphene were analyzed critically together with the numerous experimental evidences denying the magnetism in these materials. The crucial experiment of Sepioni et al [40] showed clearly that no ferromagnetism was detected in pure graphene at any temperature down to 2 K. Neither do they found strong paramagnetism expected due to the massive amount of edge defects. Rather, graphene is strongly diamagnetic, similar to graphite. Thus the possible traces of a quasi-magnetic behavior which some authors observed in their samples may be attributed rather to induced magnetism due to the impurities, defects, etc. On the basis of the present analysis the conclusion was made that the thorough and detailed experimental studies of these problems only may shed light on the very complicated problem of the magnetism of carbon-based materials.

**Keywords:** Carbon-based materials; pure graphene; the magnetism of carbon-based materials; intrinsic magnetism; induced magnetism; ferromagnetism, paramagnetism, diamagnetism; quasi-magnetic behavior; quantum theory of magnetism; the role of the low dimensionality.

Many new growth points in magnetism have appeared in the last decades. Magnetic materials, as a rule, can be metals, semiconductors or insulators which contain the ions of the transition metals or rare-earth metals with unfilled shells. According to Pauli exclusion principle the electrons with parallel spins tend to avoid each other spatially. One can say that the Pauli exclusion principle lies in the foundation of the quantum theory of magnetic phenomena. It is worth noting that the magnetically active electrons which form the magnetic moment can be localized or itinerant (collectivized).

The search for macroscopic magnetic ordering in exotic materials and artificial devices has attracted big attention [1, 2, 3, 4, 5, 6]. In particular, the carbon-based materials were pushed into the first row of researches. The understanding and control of the magnetic properties of carbon-based materials may be of fundamental relevance in applications in nano- and biosciences.

Carbon materials are unique in many ways [7, 8]. They are characterized by the various

---

<sup>1</sup>Report presented at the International Conference "DUBNA-NANO 2012", Dubna 9 - 14 July 2012, Russia.

allotropic forms that carbon materials can assume [8], including the graphene - a monolayer of carbon atoms densely packed in a honeycomb lattice [9, 10]. It was conjectured that in addition to its transport properties a rich variety of magnetic behavior may be expected in graphene, including even a kind of intrinsic ferromagnetism. Some hypothesis were claimed that connected possible spin-ordering effects with the low-dimensionality and Dirac-like electron spectrum of graphene, thus inspiring a new kind of magnetism without magnetic ions.

In spite of the fact that magnetism is not usually expected in simple  $s - p$  oxides like  $MgO$  or in carbons like graphite it was supposed that basic intrinsic defects in these systems [11, 12, 13] can be magnetic in ways that seem to be shared by more complex oxides. Moreover, a "room-temperature ferromagnetism of graphene" was claimed [14]. However, the mechanism of ferromagnetism in carbon-based materials, which contain only  $s$  and  $p$  electrons in contrast to traditional ferromagnets based on  $3d$  or  $4f$  electrons, is rather unclear.

There are many examples of physical systems with a permanent magnetic moment in the ground state [15]. These systems are the atoms, molecules and ions with an odd number of electrons, some molecules with an even number of electrons ( $O_2$  and some organic compounds) and atoms (ions) with an unfilled ( $3d-$ ,  $4f-$ ,  $5f-$ ) shells. Strong magnetic materials as a rule include  $3d-$  ions with unfilled shells [16]. (For example,  $T_C(Fe) \approx 1040K$  whereas  $T_C(Gd) \approx 290K$ ).

Thus the natural question arises: can carbene-based materials be magnetic in principle and what is the mechanism of the appearing of the magnetic state from the point of view of the quantum theory of magnetism?

Previously, the "hybrid materials" known as molecular ferromagnets in which organic groups are combined with transition metal ions were prepared [17, 18]. Here the organic groups were themselves not magnetic but were used to mediate the magnetism between transition metal ions. Organic ferromagnetism was first achieved using organic radicals called nitronyl nitroxides. Many organic radicals exist which have unpaired spins, but few are chemically stable enough to assemble into crystalline structures. Nevertheless, it was recognized that "reports of weak magnetization in organic materials have often proved to be wrong".

Magnetism in carbon allotropes has indeed been a fundamental and also controversial problem for a long time [7, 8]. Conventional wisdom has it that carbon (containing only  $s$  and  $p$  electrons) does not have a spontaneous magnetic moment in any of its allotropes. In spite of the fact that carbon is diamagnetic ( $\chi \sim -6 \cdot 10^{-6}$ ), in 2001 an "observation of strong magnetic signals in rhombohedral pristine  $C^{60}$ , indicating a Curie temperature  $T_C$  near 400-500K" was reported [19, 20]. Polymerization of fullerenes can be realized through high-pressure and temperature treatments and through irradiation with UV light. It can also occur through reactions with alkali metals. Wood *et al* described the "ferromagnetic fullerene" [21]. This new magnetic forms of  $C^{60}$  have been identified with the state which occur in the rhombohedral polymer phase. The existence of previously reported ferromagnetic rhombohedral  $C^{60}$  was confirmed. This property has been shown to occur over a range of preparation temperatures at 9 GPa. The structure was shown to be crystalline in nature containing whole undamaged buckyballs. Formation of radicals is most likely due to thermally activated shearing of the bridging bond resulting in dangling bond formation. With increasing temperatures this process occurs in great enough numbers to trigger cage

collapse and graphitization. The magnetically strongest sample was formed at 800 K, and has a saturated magnetization at 10 K, in fields above 3 kOe, of 0.045 emu g.

Moreover, in paper [22] the observation of the ferromagnetically ordered state in a material obtained by high-pressure high-temperature treatment of the fullerene  $C^{60}$  was confirmed. It had a saturation magnetization more than four times larger than that reported previously. From their data the considerably higher value of  $T_C \approx 820$  K was estimated [22].

The widely advertized "discovery" of a ferromagnetic form of carbon [19, 20, 21] stimulated huge stream of the investigations of the carbon-based materials [19, 20, 21, 22, 23, 24, 25, 26, 27, 39]. However, difficulties to reproduce those results and the unclear role of impurities casted doubts on the existence of a ferromagnetic form of carbon.

And nevertheless, it was claimed that "the existence of carbon-based magnetic material requires a root-and-branch rework of magnetic theory". Moreover, "the existing theory for magnetism in elements with only  $s$  and  $p$  electron orbits (such as carbon)" should be reconsidered in the light of the fact that there are many publications "describing ferromagnetic structures containing either pure carbon or carbon combined with first row elements", in spite of "these reports were difficult to reproduce".

It is worth mentioning that in the publications [19, 22, 23] the characterization of the samples was not made properly. This fact was recognized by the authors themselves [28, 29, 30]. In paper [29] a  $C^{60}$  polymer has been characterized for the first time with respect to impurity content and ferromagnetic properties by laterally resolved particle induced X-ray emission and magnetic force microscopy in order to prove the existence of intrinsic ferromagnetism in this material. In the sample studied the main ferromagnetic impurity found was iron with remarkable concentration. In spite of that fact authors insisted that they were able "to separate between the intrinsic and extrinsic magnetic regions and to directly prove that intrinsic ferromagnetism exists in a  $C^{60}$  polymer".

In 2004 the band structure calculations of rhombohedral  $C^{60}$  performed in the local-spin-density approximation were presented [31]. Rhombohedral  $C^{60}(Rh - C^{60})$  is a two-dimensional polymer of  $C^{60}$  with trigonal topology. No magnetic solution exists for  $Rh - C^{60}$  and energy bands with different spins were found to be identical and not split. The calculated  $C 2p$  partial density of states was compared to carbon K-edge X-ray emission and absorption spectra and showed good agreement. It was concluded that the rhombohedral distortion of  $C^{60}$  itself cannot induce magnetic ordering in the molecular carbon. The result of magnetization measurements performed on the same  $Rh - C^{60}$  sample corroborates this conclusion. It is worth noting that in majority publications on the possible ferromagnetism of carbon-based "magnetic" material the effects of the low dimensionality [32, 33] on the possible magnetic ordering were practically ignored.

In 2006 a retraction letter [34] has been published. Some of the authors (two of them decline to sign this retraction) recognized that reported high-temperature ferromagnetism in a polymeric phase of pure carbon that was purportedly free of ferromagnetic impurities was an artefact. Other measurements made on the same and similar samples using particle-induced X-ray emission (PIXE) with a proton microbeam have indicated that these had considerable iron content. Also, polymerized  $C^{60}$  samples mixed with iron before polymerization had a similar Curie temperature (500 K) to those they described [19], owing to the presence of the compound  $Fe_3C$  (cementite). In addition, it has since been shown that the pure rhombohedral  $C^{60}$  phase is not ferromagnetic [31]. Nevertheless, they concluded that "magnetic order in impurity-free graphitic structures at room temperature has been

demonstrated independently (before and after publication of ref. [19]). Ferromagnetic properties may yet be found in polymerized states of  $C^{60}$  with different structural defects and light-element ( $H, O, B, N$ ) content”.

In spite of this dramatic development, the search for magnetic order at room temperature in a system without the usual  $3d$  metallic magnetic elements continues. It was conjectured that the graphite structure with defects and/or hydrogen appears to be one of the most promising candidates to find this phenomenon.

The irradiation effects for the properties of carbon-based materials were found substantial. Some evidence that proton irradiation on highly oriented pyrolytic graphite samples may triggers ferro- or ferrimagnetism was reported [36]. The possibility of a magnetism in graphene nanoislands was speculated and a defective graphene phase predicted to be a room temperature ferromagnetic semiconductor was conjectured as well.

In paper [35] vacancies and vacancy clusters produced by carbon ion implantation in highly oriented pyrolytic graphite, and their annealing behavior associated with the ferromagnetism of the implanted sample were studied using positron annihilation in conjunction with ferromagnetic moment measurements using a superconducting quantum interferometer device magnetometer. Author’s results give some indication that the ”magnetic moments” may be correlated to the existence of the vacancy defects in the samples and this is supported by theoretical calculations using density functional theory. The possible mechanism of magnetic order in the implanted sample was discussed. Authors [35] claimed that ”it has become evident . . . that even pure carbon can show substantial paramagnetism and even ferromagnetism”.

In paper [37] recently obtained data were discussed using different experimental methods including magnetoresistance measurements that indicate the existence of metal-free high-temperature magnetic order in graphite. Intrinsic as well as extrinsic difficulties to trigger magnetic order by irradiation of graphite were discussed. The introduction of defects in the graphite structure by irradiation may be in principle a relevant method to test any possible magnetic order in carbon since it allows to minimize sample handling and to estimate quantitatively the produced defect density in the structure. The main magnetic effects produced by proton irradiation have been reproduced in various further studies. X-ray magnetic circular dichroism (XMCD) studies on proton-irradiated spots on carbon films confirmed that the magnetic order is correlated to the  $\pi$ -electrons of carbon only, ruling out the existence of magnetic impurity contributions. The role of defects and vacancies continues to be under current intensive study.

In paper [13], by means of near-edge x-ray-absorption fine-structure (NEXAFS) and bulk magnetization measurements, it was demonstrated that the origin of ferromagnetism in  $^{12}C^+$  ion implanted highly oriented pyrolytic graphite (HOPG) is closely correlated with the defect electronic states near the Fermi level. The angle-dependent NEXAFS spectra imply that these defect-induced electronic states are extended on the graphite basal plane. It was concluded that the origin of electronic states to the vacancy defects created under  $^{12}C^+$  ion implantation. The intensity of the observed ferromagnetism in HOPG is sensitive to the defect density, and the narrow implantation dosage window that produces ferromagnetism should be optimized.

In paper [38], electronic and structural characterization of divacancies in irradiated graphene was investigated. Authors provided a thorough study of a carbon divacancy, a point defect expected to have a large impact on the properties of graphene. Low-temperature scanning

tunneling microscopy imaging of irradiated graphene on different substrates enabled them to identify a common twofold symmetry point defect. Authors performed first-principles calculations and found that the structure of this type of defect accommodates two adjacent missing atoms in a rearranged atomic network formed by two pentagons and one octagon, with no dangling bonds. Scanning tunneling spectroscopy measurements on divacancies generated in nearly ideal graphene showed an electronic spectrum dominated by an empty-states resonance, which was ascribed to a nearly flat, spin-degenerated band of  $\pi$ -electron nature. While the calculated electronic structure rules out the formation of a magnetic moment around the divacancy, the generation of an electronic resonance near the Fermi level reveals divacancies as key point defects for tuning electron transport properties in graphene systems. Thus the situation is still controversial [37].

High-temperature ferromagnetism in graphene and other graphite-derived materials reported by several workers [14, 39] has attracted considerable interest. Magnetism in graphene and graphene nanoribbons is ascribed to defects and edge states, the latter being an essential feature of these materials [12]. Room-temperature ferromagnetism in graphene [39] is affected by the adsorption of molecules, especially hydrogen. Inorganic graphene analogues formed by some layered materials also show such ferromagnetic behavior [39]. Magnetoresistance observed in graphene and graphene nanoribbons is of significance because of the potential applications.

The problem of possible intrinsic magnetism of graphene-based materials was clarified in paper [40]. The authors have studied magnetization of graphene nanocrystals obtained by sonic exfoliation of graphite. No ferromagnetism was detected at any temperature down to 2 K. Neither do they found strong paramagnetism expected due to the massive amount of edge defects. Rather, graphene is strongly diamagnetic, similar to graphite. Their nanocrystals exhibited only a weak paramagnetic contribution noticeable below 50 K. The measurements yield a single species of defects responsible for the paramagnetism, with approximately one magnetic moment per typical graphene crystallite.

However, the researchers [41] found a new way to interconnect spin and charge by applying a relatively weak magnetic field to graphene and found that this causes a flow of spins in the direction perpendicular to electric current, making a graphene sheet magnetized. The effect resembles the one caused by spin-orbit interaction but is larger and can be tuned by varying the external magnetic field. They also show that graphene placed on boron nitride is an ideal material for spintronics because the induced magnetism extends over macroscopic distances from the current path without decay.

In summary, in the present work, the problem of the existence of carbon-based magnetic material was analyzed and reconsidered to elucidate the possible relevant mechanism (if any) which may be responsible for observed peculiarities of the "magnetic" behavior in these systems, having in mind the quantum theory of magnetism criteria. The origin of magnetism lies in the orbital and spin motions of electrons and how the electrons interact with one another [16, 33]. The basic object in the magnetism of condensed matter is the magnetic moment. The magnetic moment in practice may depend on the detailed environment and additional interactions such as spin-orbit, screening effects and crystal fields. On the basis of this analysis the conclusion was made that the thorough and detailed experimental studies of this problem only may lead us to a better understanding of the very complicated problem of magnetism of carbon-based materials.

## References

- [1] Roduner E 2006 *Nanoscopic materials: size-dependent phenomena* (Cambridge: Royal Society of Chemistry)
- [2] Stohr J and Siegmann H C 2006 *Magnetism. From Fundamentals to Nanoscale Dynamics* (Berlin: Springer)
- [3] Stefanita C G 2008 *From Bulk to Nano: The Many Sides of Magnetism* (Berlin: Springer)
- [4] Coey J M D 2009 *Magnetism and Magnetic Materials* (Cambridge: Cambridge University Press)
- [5] Spaldin N A 2011 *Magnetic Materials. Fundamentals and Applications* 2nd ed (Cambridge: Cambridge University Press)
- [6] Stefanita C G 2012 *Magnetism. Basics and Applications* (Berlin: Springer)
- [7] Haddon R C 1995 *Nature* **378** 249
- [8] Hirsch A 2010 *Nature Materials* **9** 868
- [9] *Graphene and Its Fascinating Attributes* 2011, ed S K Pati, T Enoki and C N R Rao (Singapore: World Scientific)
- [10] Katsnelson M I 2012 *Graphene: Carbon in Two Dimensions* (Cambridge: Cambridge University Press)
- [11] Stoneham M 2010 *J. Phys. Condens. Matter* **22** 074211
- [12] Yazyev O V 2010 *Rep. Prog. Phys.* **73** 056501
- [13] He Zhoutong *et al.*, 2012 *Phys. Rev. B* **85** 144406
- [14] Yan Wang *et al* 2009 *Nano Letters* **9** 220
- [15] Koroleva L I and Khapaeva T M 2007 *Phys. Lett. A* **371** 165
- [16] Kuzemsky A L 2009 *Physics of Particles and Nuclei* **40** 949
- [17]  *$\pi$ -Electron Magnetism: From Molecules to Magnetic Materials* 2001 (Structure and Bonding vol.100) ed J Veciana and D Arcon (Berlin: Springer)
- [18] Blundell S J and Pratt F L 2004 *J. Phys.: Condens. Matter* **16** R771
- [19] Makarova T L *et al* 2001 *Nature* **413** 690
- [20] Hohne R and Esquinazi P 2002 *Adv. Mater.* **14** 753
- [21] Wood R A *et al* 2002 *J. Phys.: Condens. Matter* **14** L385
- [22] Narozhnyi V N *et al* 2003 *Physica B* **329-333** 1217

- [23] Han K H *et al* 2003 *Carbon* **41** 785
- [24] Makarova T L 2004 *Semiconductors* **38** 615
- [25] Esquinazi P *et al* 2005 *Phase Transitions* **78** 175
- [26] Esquinazi P and Hohne R 2005 *JMMM* **290-291** 20
- [27] *Carbon-based Magnetism: An Overview of the Magnetism of Metal Free Carbon-based Compounds and Materials* 2006, ed T Makarova and F P Parada (Amsterdam: Elsevier)
- [28] Han K H *et al* 2003 *Carbon* **41** 2425
- [29] D. Spemann *et al* 2003 *Nuclear Instruments and Methods in Physics Research B* **210** 531
- [30] Makarova T L *et al* 2005 *Nature* **436** 1200
- [31] Boukhvalov D W *et al* 2004 *Phys. Rev. B* **69** 115425
- [32] Mayama H and Naito T 2009 *Physica E* **41** 1878
- [33] Kuzemsky A L 2010 *Int. J. Mod. Phys. B* **24** 835
- [34] Makarova T L *et al* 2006 *Nature* **440** 707
- [35] Rode A V *et al* 2009 *Carbon* **47** 1399
- [36] Esquinazi P *et al* 2005 *Phys. Rev. Lett.* **91** 227201
- [37] Esquinazi P *et al* 2010 *JMMM* **322** 1156
- [38] Ugeda M M *et al.*, 2012 *Phys. Rev. B* **85** 121402(R)
- [39] Rao C N R *et al* 2012 *Chem. Sci.* **3** 45
- [40] Sepioni M *et al* 2010 *Phys. Rev. Lett.* **105** 207205
- [41] Abanin D A *et al* 2011 *Science* **332** 328