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Magnetic Carbon Nanostructures?

The label *carbon nanostructure magnetism* joins two notions that do not seem to go together easily, *carbon* and *magnetism*. The main carbon allotropes, after all, are known to be non-magnetic. This appears to be true not only about the well-known solid phases diamond and graphite, but also with respect to the nanoscopic phases manufactured first in the eighties of the last century, and later: fullerenes and carbon nanotubes, single- and few-layer graphene. While intrinsic magnetism is the rule in the d- and f-blocks of the periodic table, it is extremely unusual in the second period, containing light elements with p electrons in their valence shells. Magnetic derivatives from carbon-based nanostructures, such as metallo-fullerenes with finite magnetic moments in their ground state have been known for decades, but the magnetism of these composites is inherited from elements different from carbon, such as lanthanide atoms with high spins localized in their 4f shells.

By the beginning of this century, however, sightings of intrinsic magnetism in carbon complexes became increasingly frequent and made headlines, not rarely heralded with adjectives like *surprising* [1], *unexpected* [2] or *exotic* [3]. While in the meantime, the initial surprise about carbon magnetism has somewhat worn off, astonishing discoveries continue to be made in this field, such as the first experimental demonstration of spin transport in graphene at the micrometer scale [4] or the first detection of strong spin-orbit coupling in carbon nanotubes [5].

On the other hand, magnetism in carbon nanostructures also continues to be a topic in tension. Foremost, the proposal of intrinsic carbon magnetism due to net magnetic moments at edges or vacant sites in carbon networks is charged with controvery. Proponents point not only at a large body of theoretical and computational work, predicting these effects (for an overview, see [6]), but also at numerous experiments that appear to confirm these predictions. Detractors call attention to the great difficulty of reliably separating signatures of intrinsic magnetism from artifacts due to small admixtures of magnetic impurities [3] and refer to the rather marginal, if not vanishing, net effects yielded by some recent experimental examinations of carbon magnetism [7].

In view of the ongoing debate, it would be premature to state that magnetism in carbon nanostructures is a firmly established discipline within condensed-matter physics or nanoscience. On some of the fundamental tenets of the field, after all, a widely accepted consensus is still lacking. Does this situation suggest that it is too early for a monograph on this subject?

In defense of the present undertaking, I point out that a wide variety of very diverse phenomena fits under the heading of magnetism in carbon nanostructures, some of them fairly traditional and well understood as the result of intense collaborative work between theorists and experimentalists, extending through more than two decades. These may be exemplified by fullerenes with embedded magnetic moieties. Further, the more recent and more disputed zones of the field contain much that touches on essential features of graphene and its derivatives. Therefore, it is of direct relevance to one of the most rapidly advancing branches of current materials science, the exploration of graphene as the first two-dimensional nanomaterial ever fabricated, with an abundance of record-setting electronic and mechanical properties. In this context, one may mention numerous theoretical and computational studies on spin effects in structurally modified or dimensionally reduced graphene where edges, vacancies, or topological defects alter the electronic band structure of the pristine material.

Perhaps more importantly, the union of carbon and magnetism promises more and more highly rewarding technological applications. Controlled fabrication of magnetic materials based on carbon appears to be beneficial in view of their lower production costs when compared with their metal counterparts, their physical and chemical stability, their ease of processing, and their biocompatibility. In all of these rubrics, magnetic carbon compounds are expected to surpass traditional (e.g. metallic) carriers of magnetism by a substantial margin. Further, as suggested by both theoretical and experimental evidence, graphene and carbon nanotubes, and species derived from these prototypes, are of major interest as media for spin transport, and therefore as elements of spintronics networks.

At the same time, the more traditional research into magnetically functionalized carbon nanostructures – hybrids between pure carbon units and magnetic metal species – continues to progress at a rapid pace. In these cases, carbon components provide templates for magnetic units and thus are instrumental for designing composites with tunable magnetic properties. Forming cages of strong cohesion, various types of carbon nanomaterials are used to protect and stabilize encapsulated magnetic subunits.

This book is intended as an introduction to the science of magnetic carbon nanostructures, presenting a comprehensive view of these materials that extends from the basic principles of their architecture to current perspectives for their future use in technology. The text is guided by a threefold motivation, corresponding to three main reasons for the great present interest in carbon-based nanomaterials with finite magnetic moments. These claim relevance as (1) novel materials with a broad range of possible applications, (2) carriers of spin currents and (3) paradigms for novel concepts in nanoscience and condensed-matter physics. A few comments on each of these items:

1. Research on carbon magnetism has identified a wide variety of novel nanosystems, many of them with highly uncommon, intriguing properties. On the most elementary level, strategies have been described to induce ground-state magnetism in carbon nanostructures with more than zero dimensions by dimensional reduction. Further, these structures have been shown to adopt magnetism upon controlled introduction of defects into their lattices, such as adatoms, impurities or vacancies. Of much higher structural complexity are three-dimensional nanoporous carbon networks that display high-temperature ferromagnetism, as exemplified by nanofoam or activated carbon fibers. The prototype of purely organic magnets based on carbon nanostructures is arguably C_{60}-TDAE, a compound consisting of fullerene in combination with an organic molecule. On the other hand, an ample diversity of magnetic metallofullerenes or metallonanotubes have been characterized, species that owe their magnetism to the presence of magnetic metal components. Besides their intrinsic interest for materials science, they are notable for their high relevance to medical therapy and diagnosis. Be it as safe vessels for toxic contrast agents, be it as highly efficient drug delivery systems, these units hold great promise to be developed into powerful instruments of nanobiotechnology.
2. Graphene appears highly suitable as a medium for spin transport. In the first place, this feature is related to the low weight of carbon, which implies weak spin-orbit as well as hyperfine coupling. Both of these interactions induce spin relaxation and decoherence, thus limiting the lifetime of propagating spins. Further, effective strategies for manipulating the spin transport properties of various carbon nanostructures have been outlined. This includes implementation of Rashba interactions, which provide the mechanism underlying the spin transistor concept. Also, for zigzag graphene nanoribbons and zigzag carbon nanotubes, it has been shown that half-metallicity, and thus spin-selective conductance, can be induced by applying external electric fields. These and other effects specific to carbon nanostructures make them appear extremely useful as carrier materials for spin currents in spintronics circuits.
3. Investigation of magnetic interactions in carbon nanostructures has given rise to the discovery of novel phenomena of basic significance for condensed-matter

physics. These are rooted in the *massless Fermion* nature of the low energy states of ideal graphene. Thus, the pioneering work on the quantum spin Hall effect in graphene by Kane and Mele [8] initialized the now-rapidly advancing research on *topological insulators* as a novel class of condensed-matter systems. Likewise, studies on the magnetotransport in graphene led to a basic understanding of phenomena related to *weak antilocalization* and *positive magnetoresistance*. Predictions based on the Dirac rather than the Schrödinger equation, and thus basic tenets of relativistic quantum electrodynamics, can be examined by analyzing graphene [9].

Chapters 2 to 6 are intended to lay a fundament for the treatment of more specific subjects in the later parts of the book. In more detail, Chapter 2 deals with basic concepts of atomic and condensed-matter magnetism, as far as it is of major relevance for this monograph. Chapter 3 provides information about methods that have been used with great success in the study of magnetic carbon nanostructures, including both computational and experimental approaches. Chapters 4 to 6 are meant to acquaint readers with the main protagonists of this text, where particular attention is paid to their elementary magnetic features. Graphene, carbon nanotubes and fullerenes are introduced by presenting their geometric and electronic, as well as basic magnetic properties. The treatment of magnetism in this segment of the text is mostly confined to the interaction between carbon nanostructures and external magnetic fields. Readers well informed about magnetic phenomena in condensed matter systems, and with customary methods to analyze them, may want to start at Chapter 4; those conversant with carbon nanostructures may skip over Chapters 4 to 6.

The essential content of this book is assembled in Chapters 7 to 12, where carbon nanostructures are discussed in terms of intrinsic magnetism, spin transport, charge transport in the presence of a magnetic field and magnetism resulting from interactions with magnetic as well as non-magnetic impurities. Emphasis is placed on graphene and carbon nanotubes, along with secondary structures derived from these systems. Since neither species is intrinsically magnetic, both of them acquire magnetism as their characteristics are manipulated. This can proceed by combining them with foreign elements, a strategy that is outlined in Chapter 12. An alternative route of adopting magnetic features is dimensional reduction. Thus, graphene assumes a ground state that combines ferromagnetic with antiferromagnetic features when the two-dimensional graphene lattice is trimmed down to one- or two-dimensional substructures, termed *zigzag graphene nanoribbons*. An analogous observation is made for carbon nanotubes of the zigzag type when their dimension drops from one to zero. These ideas are outlined in Chapter 7, where the emergence of magnetic phases from edge structures, as well as geometric irregularities such as vacancies in the graphene network or topological defects, is considered. Chapter 8 focuses on spin-orbit coupling. Due to the symmetries of the hexagonal lattice, this effect is predicted to be of second order, and extremely small in graphene. *Rashba interaction*, however, blending the spin-orbit with the Stark effect, makes it possible to tune the former by use of an external electric field. Carbon nanotubes display significantly stronger spin-orbit coupling than graphene, which is a consequence of their curvature and, ultimately, the different mirror symmetry operations valid for the two nanostructures.

Chapters 9 and 10 focus on spin transport phenomena. The present attention paid to this topic and the recent achievements in predicting and detecting spin currents in carbon-based materials are guided mainly by practical interest, namely the potential use of these materials for applications in spintronics. Thus, the small size of the spin-orbit coupling in graphene gives rise to the expectation of long spin relaxation times in this medium, which is essential for controlled operations involving spin currents. Techniques have been identified for how to generate and observe pure spin currents in graphene, and the experimental proof of principle for the effectiveness of these techniques has been given.

Further, carbon nanotubes are of great relevance as nanoelectronic transmission devices. Their enormous mechanical strength and flexibility in conjunction with their supreme electrical properties, including current densities that exceed those of regular metals by a factor of about a thousand, make them highly promising as elements of nanocircuitry. Importantly, the basic geometric and topological features of the tubes, namely their diameter and their chirality, allow for sensitive tuning of their electronic characteristics. Here we consider nanotubes as potential components of spintronics circuits, and especially their use as quantum dots with various spin-related properties that facilitate effective manipulation of their conductance, such as the Pauli blockade effect. These items are presented in Chapter 10, while Chapter 9 summarizes some essential tenets of spintronics, including a basic description of spin circuit elements, among them spin valves, transistors and filters, and also touches on mechanisms of generating, controlling and observing spin currents.

Chapter 11 turns to charge transport through graphene and carbon nanotubes in the presence of a magnetic field. As a magnetic field may be used as a tool to adjust the gap between the valence and the conduction band of graphene-based nanosystems, it can exert a dramatic effect on their conductivity. This is manifested by the magnetoresistance of graphene as well as carbon nanotubes, i.e. the capacity of the external field to either enhance or reduce the electric resistance of the considered nanosystem. The key for understanding magnetoresistance lies in the phenomenon of *weak localization*. This mechanism turns out to cause opposite effects in carbon nanotubes and in graphene, as the former systems tend to display negative magnetoresistance while positive magnetoresistance prevails in the latter. The root for this difference is found in the pseudospinor nature of electronic states close to the Fermi energy of graphene. Another experimentally accessible consequence of this feature is the emergence of an *anomalous quantum Hall effect* in graphene. In this context, we will trace the origin of conductivity quantization in graphene and motivate the peculiar structure of the conductivity levels. The chapter closes with an extension of these arguments to spin transport, providing a survey of the *quantum spin Hall effect* in graphene.

The remainder of this monograph deals with composite and hybrid systems, consisting of carbon nanomaterials in combination with foreign units (Chapters 12 and 14) and extended structures based on carbon allotropes (Chapter 13). A survey of magnetic metallofullerenes is followed by an account on fullerenes enclosing group V atoms (N or P). We motivate the relevance of the hyperfine interaction between the nucleus and the electronic shell of the encapsulated atom for potential implementations of fullerene-based qubits, units of quantum information. We further highlight extended fullerene structures intercalated with alkali atoms (*fullerides*) or organic molecules, most prominently tetrakis-dimethylamino-ethylene (TDAE). The uniting viewpoint in these cases is electron transfer from the guest species to the fullerene moiety, giving rise to a magnetic ground state. The particular interest of the compound TDAE-C_{60} lies in the trait that, here, the combination of non-magnetic components gives rise to a magnetic whole. Our presentation of graphene in conjunction with impurities focuses on the magnetic properties of the widely studied hydrogenated and fluorinated phases of graphene. We further comment on carbon nanotubes with added magnetic metal atoms or nanoparticles and on designs that involve these aggregates as spintronics transmission elements.

Chapter 13 treats carbon networks assembled from the structural motives of the primary carbon allotropes. Examples are provided by nano-onions (fullerenes or fullerene-analogous shells nested into each other) or by graphite and diamond shrunk to nanoscopic size. *Carbon nanofoam*, in contrast, has been understood as a carbon allotrope in its own right. It is composed of elements with open or hyperbolic geometry and thus the converse of fullerenes, which are formed from closed, elliptic clusters. Like the other networks discussed in this chapter, carbon nanofoam is characterized by surprising magnetic features that turn out to be correlated with its geometric structure.

The final chapter of this volume outlines the potential use of various magnetic carbon nanostructures for clinical purposes. These materials have turned out to be of major interest for both diagnosis and therapy. Examples for the former type of application are provided by carbon-based contrast agents for magnetic resonance imaging (MRI), such as metallofullerenes that enclose lanthanide atoms or clusters with high magnetic moments. This concept promises to unite high contrast efficiency with the safety afforded by locking the highly toxic metal component into the stable enclosure of the fullerene shell. Of equal relevance is the therapeutic usage of magnetic carbon nanosystems. Taking advantage of their response to magnetic stimuli, one employs external magnetic fields to guide them toward a specific site within the organism, which is the idea underlying the concept of *magnetic delivery*. Magnetic elements can also be used in the service of thermotherapy, which exploits the sensitivity of cancerous cells to elevated temperatures. Thus it is possible to induce hysteresis losses in magnetically loaded carbon-based nanoparticles, turning them into local sources of heat that counteract the cancerous growth. The very auspicious and very diverse biomedical strategies involving magnetic carbon nanostructures have spurred extensive research with the aim of developing them into clinical tools and, by the same token, enhancing their biocompatibility.

As might be inferred from this brief summary, the topics discussed in this book touch on most of the defining features of carbon nanostructures, attesting to the fundamental nature of carbon magnetism. This field is fundamental, as it builds on the basic physics and chemistry of carbon nanomaterials and, most importantly, keeps raising essential yet unanswered questions about these materials.