Review Report on PhD Thesis

Faculty: Central European Institute of Technology
Brno University of Technology in Brno

Academic year: 2023/2024

Student: Jorge Andres Navarro Giraldo

Doctoral study program: Advanced Materials and Nanosciences

Field of study: Advanced nanotechnologies and microtechnologies

Supervisor: doc. Dr. Ing. Petr Neugebauer, Ph.D.

Reviewer: Dr. Mark-Oliver Goerbig

PhD thesis title: Theoretical study of low energy excitations in reduced dimensionality materials

Topicality of doctoral thesis:

The thesis manuscript presented by Jorge Andres Navarro Giraldo covers several aspects of modern graphene- and graphite-based electronic and optical properties. It is mainly theoretical with a strong connection to experiments, especially in the magneto-optical domain. It covers three subfields : (i) a theoretical analysis of high-field properties of graphite, where an instability towards spin-density formation is theoretically analysed in quasi-one-dimensional Landau bands ; (ii) an experimental study of weak localisation in graphene in the prospect of an optical sub-THz identification of this phenomenon, which is more commonly explored in magneto-transport measurements ; (iii) a numerical (ab initio) study of (clusters of) single-molecule magnets on epitaxial mono- and bilayer graphene. All topics are strongly relevant in modern quantum-materials sciences on the nanoscale and may have a strong impact in the respective fields.

Meeting the goals set:

The first part of the thesis deals with a theoretical analysis of a magnetic-field-induced spin-density-wave (SDW) in graphite, within a self-consistent mean-field approach. After a proof (on the mean-field level) of the stability of such a phase, a first-order phase transition has been identified, which could be experimentally identified via hysteretic behaviour. From a technical point of view, this SDW arises from the effective one-dimensional (1D) character of the Landau bands: while the motion of the electrons in

graphite is Landau-quantised in the plane perpendicular to the applied magnetic field, the motion along the magnetic field remains free so that the wave vector in this direction is a good quantum number, and one finds a family of 1D bands. Due to the trivial nesting in 1D of the wave vector, the Fermi surface being reduced to single points, one therefore expects a density-wave instability with a periodicity given by the nesting vector. There exist indeed experimental signatures in magnetotransport at high magnetic field for such density-wave instabilities that have been the motivation of the present work. The main interest of the present theoretical work is yet beyond such transport signatures, within more direct optical spectroscopic means. Indeed, it is shown that the SDW has a magneto-optical signature in the optical conductivity, which has been calculated with the help of the Kubo formula and that could be measured in optical reflection measurements.

The second part presented in the thesis manuscript deals with weak localisation in mono- and bilayer graphene on epitaxial SiC samples. Weak localisation arises due to the destructive interference of closed quantum paths related by time-reversal symmetry that lower the conductance with respect to its classical value. This destructive interference is lifted when a (weak) magnetic field is applied to the sample so that the two time-reversal-symmetry related paths are dephased. This yields an effective increase of the conductance or decrease of the resistance as a function of the magnetic field. The effect is a prominent example of diffusive coherent electron transport in mesoscopic quantum physics, and it is commonly used to obtain access to the characteristic phase coherence time (average time between two inelastic scattering events) in DC transport measurements. The aim of this part of the thesis is to search for spectroscopic signatures of weak localisation namely in the AC conductivity in the sub-THz regime. While no full-fletched theory for a spectroscopic analysis of weak localisation has yet emerged, I find the preliminary results presented in the present thesis very interesting. They show that there is indeed a correlation between the phase coherence time and a spectroscopic response (absorption peaks). This correlation yet needs to be understood via further theoretical and experimental studies. On the experimental level, a systematic investigation of the peak structure as a function of temperature seems to be imposing itself for future studies since the phase coherence time (and length) is known to be delimited by both electron-phonon and electron-electron interactions that have a strong temperature dependence. Finally, one might suspect that epitaxial graphene is perhaps not the best adapted device to study the spectroscopic signature of weak localisation, as compared to the cleaner exfoliated or CVD-grown graphene samples encapsulated by hexagonal boron-nitride. A discussion about this point may be part of the oral defense.

The third part deals with a more applied question of nanoscopic quantum devices in the form of single-molecule magnets (SMMs) on a graphene substrate. These molecules contain cobalt as the magnetic atom, and three different Co-based compounds have been investigated. Here, the idea was to investigate, via numerical ab initio methods, the charge transfer from the adsorbed molecules to the graphene sample as well as the modification of the magnetic properties of the (SMMs). From a technical point of view, it was shown that dipole corrections play an important role in the correct description of the above-mentioned charge transfer even if their impact on the total energy as a function of the distance between molecule and graphene layer may be negligible. The effective charge transport is that of electrons from the molecules to the graphene layer (n doping), as it has also been confirmed experimentally by Raman spectroscopy. As a consequence of the electronic depletion of the (highest occupied molecular orbital of the) molecules, the magnetic moment of the latter is enhanced. Within this numerical calculation, three diffferent molecular compounds in four configurations each (orientation with respect to the graphene sheet) have been studied. Depending on the compound and its configuration,

the relative enhancement of the magnetic moment can be on the order of ~3%, and it is indeed shown to be correlated with the relative charge transfer from the molecule to the graphene sheet, which is itself on the order of up to ~8%. To make a connection with experiments, these studies need to be upscaled since optical microscope images show that the graphene sheet is covered by crystallites of these molecules with a lateral size on the order of some microns. In order to take into account a possible collective behaviour of these SMMs, an exchange-type interaction between them has been considered, and it was found numerically that the coupling is antiferromagnetic (albeit anisotropic).

Problem solving and dissertation results:

Jorge Andres Navarro Giraldo has used a large variety of techniques to obtain his scientific results, ranging from analytical self-consistant mean-field calculations (part i) to numerical DFT calculations (part iii). Furthermore – this is rather uncommon for a theoretician – he has also performed experimental studies in the characterisation of graphene samples (part ii). The results he obtained in all three parts are sufficiently important and novel for a good PhD thesis. Only the results obtained in part (ii) on the identification of weak localisation in graphene via sub-THz optical means remain on a somewhat preliminary albeit interesting level. It has been shown that there occurs an anomalous AC response at frequencies that correspond to the pertinent dephasing rates. However, as it is honestly pointed out in the manuscript, there is not yet a full-fletched theory or understanding of this correlation, and I am convinced that the presented results are an important step towards such a deeper understanding and a spectroscopic identification of weak localisation.

Importance for practice or development of the discipline:

All three parts of the thesis are important to different degrees in their respective subfields. While the first part of the thesis has not yet been published in a scientific review, I am convinced that the quality and the relevance of the obtained results warrent publication. As mentioned above, the calculated magneto-optical signature of the expected high-field SDW phase may guide experimentalists in the identification of such a phase. Because the presently existing indications from magnetotransport are relatively indirect, such spectroscopic measurements may provide further relevant insight. As mentioned above, the second part consists of a very interesting complementary identification of weak localisation via spectroscopic means (AC transport in the sub-THz range) with respect to usual electric quantum transport. The presented results are a relevant milestone in a to be completed theoretical framework. The last part presents already published work on magnetic nanodevices based on SMMs on a graphene substrate and may guide further experimental studies in this field and more applied device fabrication.

Formal adjustment of the thesis and language level:

The thesis manuscript is overall very well written and accessible to read. I have particularly appreciated the very pedagogical introductions to the different fields. The results are very clearly exposed. As a minor criticism, I am sometimes missing a more substantial motivation of the different (sub)fields in

which the present research is embedded. As an example, weak localisation (in graphene as well as in other diffusive coherent conductors) is now a rather mature phenomenon in the field of quantum mesoscopic physics, and it is commonly used in the measurement of dephasing times or rates. The manuscript might benefit from a more involved discussion of the possible advantages presented by a spectroscopic identification of weak localisation as compared to established quantum transport.

Questions and comments:

In order to prepare the oral defense, here are some questions that may be discussed then. As for the first part, my main comment would be about the motivation to study only SDWs. While an SDW instability is indeed a reasonable expectation, we know generally from 1D or quasi-1D systems that they have a generic tendency to all types of instabilities as a consequence of their reduced dimension. The even simpler hypothesis would be a simple charge-density wave (CDW). I am quite sure that this would also be a possible mean-field solution, or elsewise a pair-density-wave that is quite intensely studied in other systems at the moment. (Such a pair-density wave could be viewed as condensed Cooper pairs at a non-zero wave vector given by the nesting vector.) Have such alternative states been considered? And if not, is it reasonable to consider them, or are their other strong reasons to favour a SDW? It might also be interesting to compare the magneto-optical signatures of such alternative density waves to those of the present SDW in order to provide a possible experimental distinction between these states.

As for the second part, I have already indicated above possible questions that may be discussed at the oral defense. What is the advantage of a spectroscopic identification of weak localisation with respect to quantum transport? What type of information can be obtained from it? Beyond these questions concerning the motivation of these studies, what are the missing ingredients – both experimentally and theoretically – for a full theory of weak-localisation spectroscopy.

Concerning the part on SMMs, my main question is concerned with the upscaling of the DFT results on SMMs with respect to the experimentally relevant situation of SMM clusters. As seen from the optical data, these clusters have a lateral extension of some microns or even tens of microns while the SMMs are compounds in the nm range, i.e. three to four orders of magnitude separate their spatial dimensions. The collective aspect is only taken into account via a Heisenberg-type nearest-neighbour interaction. This is indeed a reasonable approach, but only if the molecules are arranged in a periodic lattice that needs to be bipartite to host an antiferromagnetic ground state. The situation is different if the arrangement is e.g. triangular or even amorphous. Are there indications about the arrangement of the molecules on the graphene sheet? And furthermore, are there not other energetic aspects that need to be taken into account beyond the nearest-neighbour interaction of the molecules namely in the coupling to the graphene substate? One may reasonably expect that the SMMs do not form a single layer on top of the graphene sheet but that there may be a multilayer structure in which case the charge transfer between the SMMs and the graphene sheet would be less efficient.

Conclusion:

In conclusion, I have appreciated reading the present PhD manuscript, which is clearly written and presents original results that are relevant in the field of quantum matter and their spectroscopic characterisation. The questions raised above are less a criticism of the presented results but rather a guideline for the oral defense which I am looking forward to with great pleasure.

In my opinion, the reviewed thesis fulfills all requirements posed on theses aimed for obtaining PhD degree. This thesis is ready to be defended orally, in front of respective committee.

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Dr. Mark-Oliver Goerbig

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