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Ph.D. Thesis booklet

Spin and Charge Dynamics in Novel Low-Dimensional Materials

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Introduction

Working of the modern society is based on the exploitation of novel technologies. The technologies were enabled by fundamental and application-oriented research in material sciences. A well-known example is that advances in manufacturing silicon with impurities below the ppb (parts per billion) concentration enabled the modern semiconductor industry, which in turn led to the advent of consumer devices. Besides, understanding fundamental phenomena in solids (including e.g. the dynamics of electron charge and spin) not only broadened our view but lead to many important applications such as e.g. in the field of superconductivity.

Albeit an old material (graphite has been known since antiquity), carbon still holds surprises due to the rich variety of allotropes which are enabled by the uniquely flexible bonding properties of carbon. This is not only the basis of life but also the basis for a variety of compelling solid-state systems, which are the subject of the present thesis.

The advent of low dimensional materials and their physics was started with the discovery of the "0D" allotrope of carbon, the C_{60} fullerene in 1985 by Kroto and his colleagues [1]. The discovery of a novel carbon allotrope, which is not present naturally on Earth, gained enormous scientific attraction. A single molecule, made up of 60 atoms of the same kind is not just interesting on paper, but also resulted in further scientific advances. It turned out that these big molecules not just form a solid crystal, but are also able to form polymeric bonds. Adding alkali atoms to the formula, it resulted in metallic and even superconducting materials, like Rb_3C_{60} [2]. The most prominent application for nowadays is the possibility to fabricate a spin qubit made up of only a single molecule [3].

The next breakthrough came in 1991 with multi-walled carbon nanotubes [4]. Just within 2 years, researchers managed to synthesize single-walled carbon nanotubes [5, 6]. The physical properties of this material reflect a truly one-dimensional behavior, as verified by the band structure [7], the presence of Van Hove singularities in the optical spectrum [8], the presence of quantized ballistic transport [9–11] and Luttinger phase [12]. Also, highly anisotropic heat conductivity is another important feature to be mentioned [13]. The most promising applications of nanotubes are gas sensing [14], flexible electronics [15], and energy storage [16].

The next step to advance a dimension further to 2D was demonstrated by Geim and Novoselov in 2004 [17] with the discovery of graphene. The planar honeycomb lattice of carbon atoms is just as exciting as the one mentioned above. The presence of massless Dirac fermions in the vicinity of the Dirac cones [18] and room temperature quantum Hall effect [19] are

only two of the many interesting physical phenomena in graphene. Recently, the topological behavior and superconductivity of bilayer graphene twisted in a magic angle, which also attracted the eyes [20, 21]. The wide range of applications stem from spintronics [22–24] and quantum computing [25] through energy storage [26, 27], energy harvesting [28] and gas sensing [29] all the way to flexible displays [30, 31], and light emitting devices [32]. Moreover, a recent study shows that graphene might find applications also in waste reprocessing [33].

Unfortunately, the third dimension does not fit into the historical timeline, as graphite has been around "since the Greeks". Even though everybody thinks that graphite is well understood, it still holds several surprises. One example is the anomalous anisotropy and temperature dependence of the *g*-factor and spin-relaxation times, which cannot be interpreted with the conventional Elliott–Yafet [34, 35] theory.

Furthermore, all the mentioned materials had and have a huge impact on organic chemistry. Modification, intercalation, and functionalization of the low-dimensional carbon allotropes are of special interest. Among the many possibilities, intercalation with lithium and sodium is of special importance, as the current need for lithium-based energy storage has skyrocketed in recent years. Moreover, the emergence of sodium-based batteries to replace current technologies is promising [36–40].

As we are closing on to the end of the famous Moore's law more and more, researchers and engineers turned from classical Turing–von Neumann computers to spintronics and quantum computers. In all of the new architectures, the spin degree of freedom is used instead of the charge to manipulate the states of a bit. The reason is, while the momentum of an electron is conserved between two collisions for about $\tau \sim 10^{-12}$ seconds only, the much weaker interactions of spins with their neighborhood yields $\tau_s \sim 10^{-8}$ seconds even if conditions are far from ideal. A simple calculation in a diffusive model results in a diffusion length of about 100 μm, which is enough to fabricate a spintronics chip. In spintronics, the computational basis is a classical boolean, where a bit can either have a state 0 or 1, but the spin transistors ("SFETs") operate with the manipulation of spins and the resulting current depends on the spin orientation. The concept is somewhat similar to how a modern hard disk is operating with the use of giant magnetic resistance (GMR); the concept of SFET can be found in Refs. [41]. In contrast, in quantum computing the superposition of the states is also allowed: $|\psi\rangle = \alpha |0\rangle + \beta |1\rangle$, where $|\alpha|^2 + |\beta|^2 = 1$ and $\alpha, \beta \in \mathbb{C}$. The new architecture requires new operations and new materials to be functional. As of 2020, we can say that we are at the beginning of the quantum era since Google managed to achieve quantum supremacy in

the recent past with a 53 qubit chip [42].

Objectives

Several open questions in the field motivated the present research. The alkali atom intercalation of carbon could be further explored, such as, what is the nature of charge dynamics on the Li_4C_{60} superionic conductor? What is the origin of the electronic contribution? Is it possible to exfoliate graphene on a large scale with acceptable quality? Is it possible to intercalate the exfoliated graphene with alkali atoms? What are the properties of the resulted materials? Can Raman spectroscopy combined with potassium intercalation reveal the maximum number of layers present in the material? Is the spin-relaxation time sufficient in these materials to be used in spintronics? What is the position of the Fermi energy in these materials?

During my work, I wished to answer these questions. I investigated the conductivity of the superionic Li_4C_{60} in the microwave frequency range. With the assistance of infrared spectroscopy and HF-ESR, I concluded the presence of both electronic and ionic conductivities in the polymeric phase. The conductivity below 125 K is dominated by the small amount of tunneling electronic defects, whose presence is confirmed by HF-ESR and conductivity measurements. I also observed the reversible breaking of polymeric bonds above 410 K.

I adapted the liquid ammonia doping method to potassium-doped SWCNTs. K doped SWCNTs prepared this way was compared against conventional vapor phase prepared samples. I found significant charge transfer in materials prepared both ways, but the intercalation was more complete for the one prepared with the liquid ammonia technique as observed by Raman spectroscopy. I noted the emergence of a new, Dysonian peak in ESR of the materials, as a result of the presence of conducting electrons and a transition to a Fermi liquid. With temperature-dependent measurements, the metallicity is confirmed and the density of states was extracted, in this sense, the resulted materials are good model systems of biased graphene. I also performed *in situ* microwave conductivity measurements, where the resistivity change of the material is followed and a transition from semiconducting to a metallic phase is observed.

I investigated the vibrational properties of few-layer graphene (FLG) prepared by liquid-phase exfoliation and with three, different mechanical processing. From the Raman results, I deduced that the ultrasound sonication yields the best quality. I confirmed this utilizing ESR experiments. Following the research, I studied the effect of potassium exposure in a

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series of *in situ* Raman experiments. I observed a split G mode in the intermediate steps and the presence of the C_z and a broad Breit–Wigner–Fano (BWF) mode in the final intercalation step. The presence of both Raman modes proves successful intercalation and the transfer of electrons to the hexagonal lattice. Analyzing the G and 2D modes in the intermediate steps, I propose a scheme of how the material is intercalated and suggest a protocol to characterize a sample using only Raman spectroscopy and potassium intercalation.

I optimized the liquid ammonia technique for the few-layer graphene to be doped with lithium and sodium. I observed a gradual color change of both materials and Raman fingerprints of the successful charge transfer. Using thermodynamic arguments I found that sodium selectively dopes the monolayer graphene flakes in the FLG material. I performed ESR experiments that confirm the presence of new conducting electrons with a finite density of states calculated from Pauli spin susceptibility. Using the ESR results I calculated the shift of the Fermi energy to be around 1 eV in both materials. From the ESR linewidth, I deduced the spin relaxation time to be in the order of 10 nanoseconds, which is adequate for spintronic applications.

Thesis Points

1. I studied the electronic and ionic conductivities in the Li_4C_{60} superionic fulleride. I carried out microwave conductivity measurements in a wide temperature range of $40 - 530$ K utilizing a He cooled cryogenic and a nitrogen cooled-heated high-temperature setup. I observed the polymeric-monomeric phase transition around 410 K and the presence of both lithium ionic and electronic conductivities at low temperatures. I observed a good agreement of 125 K with previous literature observations for the freeze-out of lithium ionic motion and extracted the activation energies for both types of charge carriers. With the assistance of high-field ESR, ^7Li NMR and calorimetric measurements, I concluded that the origin of the electronic contribution is the presence of a small amount of charged defects. Furthermore, I proved that the conductivity of the monomeric phase becomes gradually higher than the polymeric, as expected. The results are published in Ref. [T1].

2. I prepared potassium-doped single-walled carbon nanotube samples utilizing liquid ammonia based alkali doping. In Raman spectroscopic measurements, I found that the nanotubes are highly charged

and display a metallic behavior as a broad Fano mode dominates the spectrum. I carried out room temperature ESR measurements and observed the emergence of a new ESR line corresponding to itinerant charge carriers. I performed microwave conductivity measurements and found that the K-SWCNT material is indeed metallic. Furthermore, I followed the evolution of metallicity upon intercalation in an *in situ* microwave conductivity measurement. The results are published in Refs. [T2, T3].

3. I characterized the chemically exfoliated few-layer graphene samples, prepared with different post-processing methods, using Raman and ESR spectroscopies together with microwave conductivity measurements. In the Raman measurements, I observed a significant difference in the materials from the starting graphite powder. I studied the changes of the D and G mode in detail and observed a singlet G mode, upshifted to that of graphite and a doublet 2D mode. The latter observation indicates that the material consists of few-layers and single-layer flakes as confirmed by AFM. I performed electron spin resonance measurements and the results prove the presence of itinerant charge carriers with g-factors higher than that of the free electron, indicating a slight p-type doping or the presence of remaining solvents. Utilizing microwave conductivity measurements, I deduced that the microwave loss is mainly determined by the grain size. Taking all the techniques into account, I concluded that ultrasound treatment results in the best quality. The results are published in Ref. [T4].

4. I carried out *in situ* intercalation experiments on the few-layer graphene system and observed a gradual change of the Raman spectrum. In the first doping steps, I observed the split of the G mode and experienced a doublet 2D mode. I also noted the rapid disappearance of the D Raman mode. In the completely intercalated material, I found the presence of the so-called C_z mode and the emergence of a Fano mode near 1505 cm^{-1}. From these, I deduced that there is an ordered lattice of potassium atoms and I found that the host FLG becomes charged. I extracted the electron-phonon coupling and found that the charge transfer is higher than in potassium-doped graphite species. Through the analysis of the G and 2D modes in the intermediate steps, I established a model of how an FLG with a mixture of different layers is intercalated. Using these findings, I suggested a protocol to determine the maximum number of layers present in the material. The results are published in Ref. [T5].

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5. I adopted and optimized the liquid ammonia-based alkali doping for few-layer graphene. I analyzed the possible side-reactions and managed to suppress their production. The latter was confirmed by the absence of Raman and ESR active modes of amides and lithium imide. The optimized technique is published in [T6]. With the optimized method, I successfully synthesized lithium and sodium intercalated few-layer graphene. I used optical microscopy and Raman spectroscopy to confirm the doping. From the Raman spectra, I observed a high degree of charge transfer, clearly denoted by the presence of a Fano mode near the G mode of the starting material. Through spectral analysis, I extracted the electron-phonon coupling, which is proportional to the amount of charge transferred, and I found that it is comparable to that of the LiC_6 graphite intercalation compound. Since graphite cannot be intercalated with sodium, here I discovered that sodium selectively dopes the single-layer flakes, and is a good marker to show whether a mixture with different number of layers in a graphene material contains single-layer flakes or not. I confirmed the presence of charge transfer to the graphene host using ESR spectroscopy. I carried out temperature-dependent measurements to prove the presence of Pauli type spins in the system. Using a simple model I also estimated the density of states and the shift of the Fermi energy in the two materials. For the latter, I found 1.1 eV, which is a large value and comparable to that of LiC_6. From the ESR linewidth, I calculated the spin-relaxation time and found values at least one order higher than in single-layer graphene, which I refer to as ultralong values. I suggest that these materials might find applications in spintronics and energy storage. The results are published in Ref. [T7].

List of Publications

[T1] D. Quintavalle, **B. G. Márkus**, A. Jánossy, F. Simon, G. Klupp, M. A. Győri, K. Kamarás, G. Magnani, D. Pontiroli, and M. Riccò, "Electronic and ionic conductivities in superionic Li_4C_{60}," *Physical Review B*, vol. **93**, no. 20, p. 205103, 2016.

[T2] P. Szirmai[†], **B. G. Márkus**[†], B. Dóra, G. Fábián, J. Koltai, V. Zólyomi, J. Kürti, B. Náfrádi, L. Forró, T. Pichler, and F. Simon, "Doped carbon nanotubes as a model system of biased graphene," *Physical Review B*, vol. **96**, no. 7, p. 075133, 2017, [†]: equal author contribution.

[T3] **B. G. Márkus**, G. Csősz, O. Sági, B. Gyüre-Garami, V. Lloret, S. Wild, G. Abellán, N. M. Nemes, G. Klupp, K. Kamarás, A. Hirsch, F. Hauke, and F. Simon, "Electronic Properties of Air-Sensitive Nanomaterials Probed with Microwave Impedance Measurements," *Physica Status Solidi B*, vol. **255**, no. 12, p. 1800250, 2018.

[T4] **B. G. Márkus**, F. Simon, J. C. Chacón-Torres, S. Reich, P. Szirmai, B. Náfrádi, L. Forró, T. Pichler, P. Vecera, F. Hauke, and A. Hirsch, "Transport, magnetic and vibrational properties of chemically exfoliated few-layer graphene," *Physica Status Solidi B*, vol. **252**, no. 11, pp. 2438–2443, 2015.

[T5] P. Szirmai†, **B. G. Márkus**†, J. C. Chacón-Torres, P. Eckerlein, K. Edelthalhammer, J. M. Englert, U. Mundloch, A. Hirsch, F. Hauke, B. Náfrádi, L. Forró, C. Kramberger, T. Pichler, and F. Simon, "Characterizing the maximum number of layers in chemically exfoliated graphene," *Scientific Reports*, vol. **9**, p. 19480, 2019, †: equal author contribution.

[T6] **B. G. Márkus**, P. Szirmai, S. Kollarics, B. Náfrádi, L. Forró, J. C. Chacón-Torres, T. Pichler, and F. Simon, "Improved alkali intercalation of carbonaceous materials in ammonia solution," *Physica Status Solidi B*, vol. **256**, no. 12, p. 1900324, 2019.

[T7] **B. G. Márkus**, P. Szirmai, K. Edelthalhammer, P. Eckerlein, A. Hirsch, F. Hauke, N. M. Nemes, J. C. Chacón-Torres, B. Náfrádi, L. Forró, T. Pichler, and F. Simon, "Ultralong spin lifetime in light alkali atom doped graphene," *ACS Nano*, 2020, *accepted, in press*.

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