Transition from insulating to conducting states in fulleride compounds

Summary of the Ph.D. thesis

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Introduction

The discovery of the C_{60} "fullerene" molecule by Curl, Kroto and Smalley in 1985 opened a new era for carbon-based materials. The high symmetry of the molecule and its unusual physical properties inspired a large number of chemical studies which resulted in the synthesis of thousands of new compounds. In 1991 the synthesis of a macroscopic amount of fullerene molecules by Krätschmer *et al.* allowed to obtain solid C_{60} raising the interest of the solid state physics community.

In 1991 Haddon and coworkers showed that the intercalation of C_{60} crystals with alkali atoms gives rise to charge transfer fulleride salts which show metallic behavior and are superconducting with relatively high transition temperatures. In 1994 Pekker *et al.* found that in alkali intercalated fullerides AC_{60} (A=K,Rb, Cs) the fullerene molecules are covalently bonded to each other forming one-dimensional polymeric chains. In the following years an intensive research resulted in the discovery of other one-, two- and three-dimensional polymeric structures.

The interplay of molecular and solid state properties in the fullerene molecular crystals results in a very rich physics. Fullerides are strongly correlated electronic systems in which even small differences in the crystalline structure strongly influences the ground state. Experimental evidence and theoretical calculations showed that even the Jahn-Teller effect which is difficult to observe in conventional materials plays an important role in the electronic properties.

Objectives

Modern high frequency ESR spectrometers allow a detailed study of solid state phases on a scale of some nanometers which is difficult to access by other experimental techniques. The combined analysis of the electron spin resonance and the temperature dependence of conductivity is a powerful method to investigate both the electronic and magnetic properties of these materials. With this approach we studied the nature of the ground state and the electronic configuration of different fulleride compounds. The Na_2C_{60} fulleride salt was believed to be an insulator due to the cooperative influence of the Jahn-Teller effect and electron-electron correlations. Experimental evidence of an insulating ground state would have been important to confirm the Jahn-Teller-Mott theory of the electronic configuration of fulleride salts with an even number of electrons per fullerene molecule. We also gain a deeper insight in the electronic properties of two fulleride polymers characterized by structural disorder: Mg_5C_{60} and $K_2C_{60}C_8H_8$.

The transport properties of the Li_4C_{60} fulleride polymer were studied in collaboration with the group of Mauro Riccó of the University of Parma (IT) and Gábor Csányi of the University of Cambridge (UK). Frequency dependent conductivity and nuclear magnetic resonance measurements combined with theoretical calculations showed that this polymer is an ionic conductor due to the diffusion of the Li^+ ions. High frequency ESR measurements performed were addressed to study of the electronic contribution to the conductivity

of this polymer.

In 2005, it was decided to increase the sensitivity of the high frequency spectrometer at the Budapest University of Technology and Economics with the acquisition of a new microwave source and replacing the wave guides by a quasi-optical bridge. Previous experience on similar experimental setups at the ESR laboratory of the EPFL university in Lausanne suggested the importance to isolate the spectrometer vibrationally from the ground. Relative displacements between the magnet and the optical bridge results, in fact, in a change of the optical path which induces a noise at the detector. For these reasons, we placed the spectrometer on a vibration-isolated supporting structure. We participated in the design of the structure in collaboration with Dr. Reis of the Building Acoustic Laboratory and Dr. Kiss and Dr. Hunyadi of the Structural Department. The design of the new elements of the spectrometer was completed in the summer of 2006. The construction of the supporting structure begins in September and ended in March 2007. The first spectrum was collected in April 2007.

Theses

1. I took part in the project to modernize the high frequency electron spin resonance (HF-ESR) spectrometer at the Budapest University of Technology and Economics. I constructed the probe head and the vibration isolated supporting structure of the spectrometer. The self resonant frequency of the structure is 10 Hz and this low value guarantees the mechanical stability needed to measure small intensity ESR signals. The sensitivity of the upgraded spectrometer, about 10^{10} spin/G at 222.4 GHz, is comparable to the best 9 GHz commercial spectrometers.

2. I measured the various phase transition temperatures of the KC_{60} fulleride with HF-ESR and microwave conductivity. I demonstrated that these experimental techniques are particularly suitable to evidence phase segregations in fullerides. The enhanced spectral resolution of the high frequency ESR allows to separate the contributions of phases with slightly different g factors which have a common line in commercial 9 GHz ESR spectrometers. The contactless microwave loss measurements allow a precise measurement of the intrinsic electric conductivity.

3. My high frequency ESR measurements evidence phase segregation on a nanoscale in the Na_2C_{60} fulleride salt below 450 K. The spin susceptibility extracted from the ESR intensity demonstrates that at least one of these phases is metallic. I showed that at higher temperatures the Na^+ ions diffuse and the material is homogeneous with a stoichiometric composition of Na_2C_{60} at 520 K. I confirmed the role of the Na^+ ion diffusion in the segregation process with HF-ESR measurements on samples quenched from temperatures above 520 K.

4. I showed with multifrequency ESR that the fulleride polymer Mg_5C_{60} is a homogeneous material, stable to at least 823 K. I performed infrared and Raman studies that suggest single bonds between the fulleride ions and possible Mg-C_{60} covalent bonds. In a combined ESR and microwave conductivity study, I showed that Mg_5C_{60} is metallic above 200 K and undergoes a gradual transition to a paramagnetic insulating state at lower temperatures. I attributed this transition to Anderson localisation of the electronic states driven by the intrinsic disorder of the crystal structure. From a study of the ESR line width I suggested that the main spin relaxation mechanism is the electron-phonon coupling.

5. I studied by microwave conductivity and ESR the effect of potassium intercalation on the electric and magnetic properties of poly($C_{60}C_8H_8$). I showed that the resulting $K_2C_{60}C_8H_8$ copolymer is metallic at $T > 200$ K, in contrast to the pristine poly($C_{60}C_8H_8$) copolymer that is an insulator at all temperatures. At lower temperatures $K_2C_{60}C_8H_8$ has a gradual transition to a magnetic insulator ground state that I attributed to a disorder-driven Anderson localization of the electronic states.

6. I showed that hopping localized electronic states contribute to the microwave conductivity of the polymeric phase of the Li_4C_{60} fulleride. I studied the effects of de-

polymerization on the microwave conductivity and showed that the monomer phase is a good conductor.

Publications related to my Ph.D. work:

1. D. Quintavalle, F. Borondics, G. Klupp, A. Baserga, F. Simon, A. Jánossy, K. Kamarás and S. Pekker: *Structure and properties of the stable two-dimensional conducting polymer* Mg_5C_{60}, Phys. Rev. B **77**, 155431 (2008).

2. D. Quintavalle, F. Simon, A. Jánossy, F. Borondics, A. Baserga, K. Kamarás and S. Pekker: *The fulleride polymer* Mg_5C_{60}, Phys. Stat. Sol. (b) **244**, 3853 (2007).

3. G. Klupp, P. Matus, D. Quintavalle, L. F. Kiss, E. Kováts, N. M. Nemes, K. Kamarás, S. Pekker and A. Jánossy: *Phase segregation on the nanoscale in* Na_2C_{60}, Phys. Rev. B **74**, 195402 (2006).

4. D. Quintavalle, F. Simon, G. Klupp, L. F. Kiss, G. Bortel, S. Pekker and A. Jánossy: *Metallic behavior in the potassium doped fullerene-cubane copolymer*, Submitted to EPJ B , 2008 (.)

Further publications:

1. S. Tóth, D. Quintavalle, B. Nafrádi, L. Korecz, L. Forró and F. Simon: *Enhanced thermal stability and spin-lattice relaxation rate of* $N@C_{60}$ *inside carbon nanotubes*, Phys. Rev. B **77**, 214409 (2008).

2. D. Quintavalle, F. Simon, A. Jánossy, F. Borondics, A. Baserga, K. Kamarás, S. Pekker: *Metallic bundles of single-wall carbon nanotubes probed by electron spin resonance.*, Phys. Stat. Sol. (b) **244**, 3885 (2007).