PhD thesis booklet

Two dimensional spin transport and magnetism in layered organic crystals

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Background

The interactions between electrons are responsible for a large number of collective physical phenomena in solids, including superconductivity, ferroelectricity and magnetism. In strongly correlated materials electron–electron interactions are important and they lead to correlations between particles. In low-dimensional systems electron-electron correlations are stronger. Many new phenomena occur in quasi-one- and two-dimensional systems which are not observed in three dimensional systems. Another benefit of low dimensional systems is that for many problems solvable theoretical models are available.

In two dimensional charge transfer salts donor molecules are arranged into layers. The crystals are built from flat organic molecules. The molecular orbitals overlap producing partially filled bands. The two dimensional organic sheets are separated by a one atomic thick anion layer and they might be conducting depending on the exact structure. The two dimensional crystal structure is mirrored in the physical properties of such systems. Their physical properties reflect the shape of the organic molecules.

A major family of the organic charge transfer slats is based on BEDT-TTF (Bis-ethylenedithio-tetrathiafulvalene, $C_{10}H_8S_8$) molecules. The BEDT-TTF molecules are arranged differently in various crystals. Depending on the arrangement and fine details of the crystal structure the crystals exhibit various groundstates. One advantage of these organic crystals is this high flexibility and variability. The interactions are easily tunable by either hydrostatic- or chemical-pressure.

In κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]X$, X=Cl, Br, (hereafter κ-ET_2-X) systems, the BEDT-TTF molecules are arranged into dimers. Every dimer caries a hole thus the conduction band is half filled. The half filled band is crucial in describing the phase diagram. The system lies on the border line of a Mott metal-insulator transition. κ-ET_2-Br shows superconducting groundstate while κ-ET_2-Cl orders antiferomagnetically at low temperatures. The superconducting ground state can be reached by applying a small, 30 MPa pressure on the κ-ET_2-Cl system.

Motivation

In my thesis I concentrate on two topics. The main field of my research was two dimensional organic conductors, but I also investigated Prussian Blue analogues.

κ-ET_2-X, X=Cl, Br is in the center of interest due to their two dimensional behavior and their rich phase diagram. Although κ-ET_2-X have been investigated for decades the importance of the interactions between adjacent layers and the nature of the superconducting ground state are still unknown. The main goal of my research was to experimentally study the strength of the interlayer interactions and thus the two-dimensionality of these systems. Most theories neglect the, eventhough they might play an important role in the development of the low temperature ground state.

At high temperatures between 50 K and 300 K the members of κ-ET_2-X are bad metals. In this temperature range my purpose was to investigate the interlayer spin diffusion among adjacent layers. I studied the two dimensionality of the spin transport in the entire pressure-temperature phase diagram. Under pressure experiments are also crucial to disentangle the effects of various interactions.

At low temperatures and at ambient pressure κ-ET_2-Cl is antiferromagnetically ordered below T_N =23 K. The AFMR (antiferromagnetic resonance) strongly depends on the magnetic interactions in the crystal. My goal was to examine the angle- and magnetic field dependence of the AFMR and to determine the value of the main interactions. This is an ideal tool to examine the magnetic interactions between the neighboring layers.

Above the Néel temperature magnetic fluctuations are observable in κ-ET_2-Cl. These fluctuations increase the ESR linewidth. We examined the effects of fluctuations at various magnitudes and orientations of the external magnetic field. Our goal was to study the correlations between fluctuations in adjacent layers and investigate how strong is their two dimensional nature.

Another part of my research concentrated on a Prussian blue analog material $RbMn[Fe(CN)_6]\cdot H_2O$. This crystal undergoes a charge transfer transition between high temperature Mn^{2+}-Fe^{3+} and low temperature Mn^{3+}-Fe^{2+} phases. My aim was to study this charge transfer transition by electron spin resonance.

Experimental methods

I performed low- and high-frequency electron spin resonance (ESR) measurements. At low frequencies I used a commercial Bruker ELEXSYS E500 spectrometer. For high frequency measurements I used spectrometers working in the 111-420 GHz frequency range at Budapest (Budapest University of Technology and Economics, Department of Physics) and at Lausanne (École Polytechnique Fédérale de Lausanne). Both high frequency spectrometers are home developed and they allow high-sensitivity measurements. Furthermore, these high-frequency spectrometers are quipped by a piston cylindrical pressure cell capable of reaching 1.6 GPa pressure.

Thesis statements

I. I developed a conduction electron spin resonance (CESR) based method to measure the interlayer spin hopping rate in quasi two dimensional crystals containing two crystallographically different layers in a unit cell. I have shown that in the temperature range of 50 K to 300 K spin transport is extremely two dimensional in κ-BEDT-TTF_2 $Cu[N(CN)_2]X$, X=Cl, Br (abbreviated κ-ET_2-X) crystals. The frequency of interlayer spin hopping is as low as $\sim 2*10^8$ Hz for both compounds. Spins diffuse within one layer for several nanoseconds to the distance of a few tenth of a micrometer.

II. I mapped the interlayer spin hopping rate throughout the pressure-temperature phase diagram of κ-ET_2-Cl. I found that the high temperature interlayer hopping rate correlates with the nature of the ground state. For κ-ET_2-Cl the interlayer hopping is slow at ambient temperature and decreases further as the Mott transition to the insulating ground state is approached. On the contrary, under pressure and in the Br compound the interlayer hopping rate increases rapidly as the low temperature superconducting state is approached.

III. I measured and interpreted the angular dependence of the antiferromagnetic resonance (AFMR) modes of κ-ET_2-Cl. I observed all four resonance modes predicted by theory in several magnetic field orientations. The isotropic exchange, the Dzyaloshinskii–Moriya antisymmetric and the weak interlayer interaction constants were determined from simulating the resonance modes. The ratio of intra- and interlayer interaction energies is as large as 10^6.

IV. I observed antiferromagnetic fluctuations in κ-ET_2-Cl above the Néel temperature. I showed that the fluctuations are due to the Dzyaloshinskii-Moriya interaction, they are two dimensional and independent in adjacent layers. Fluctuations lie in the plane perpendicular to the Dzyaloshinskii–Moriya vector and increase with increasing external field. Contrary to earlier suggestions, the Néel temperature of the three dimensional magnetic order is unchanged by the magnetic field.

V. I studied by ESR the Prussian Blue analogue $RbMn[Fe(CN)_6] \cdot H_2O$ that displays a possibly technologically important charge transfer transition. I observed superparamagnetic clusters related to defects. The clusters are weakly to the bulk. The ESR of the bulk was not found at any temperatures which is explained by a rapid spin relaxation. We suggested that even at high temperatures the dominant Mn^{2+}-Fe^{3+} ionic state contains an admixture of the low temperature Mn^{3+}-Fe^{2+} state.

Publications related to my thesis statements:

1. Á. Antal, T. Fehér, E. Tátrai-Szekeres, F. Fülöp, B. Náfrádi, L. Forró, A. Jánossy, Pressure and temperature dependence of interlayer spin diffusion and electrical conductivity in the layered organic conductors κ-$(BEDT\text{-}TTF)_2Cu[N(CN)2]X$, (X=Cl, Br), Phys. Rev. B **84**, 075124 (2011)

2. Á. Antal, A. Jánossy, L. Forró, E.J.M. Vertelman, P.J. van Koningsbruggen and P.H.M. van Loosdrecht, Origin of the ESR spectrum in the Prussian Blue analogue $RbMn[Fe(CN)_6]H_2O$, Phys Rev B **82**, 014422 (2010)

3. Á. Antal T. Fehér, B. Náfrádi, R. Gaál, L. Forró, A. Jánossy, Measurement of interlayer spin diffusion in the organic conductor κ-$(BEDT\text{-}TTF)_2Cu[N(CN)2]X$, X=Cl, Br, Physica B, **405**, 10.1016, (2010)

4. Á. Antal, T. Fehér, A. Jánossy, E. Tátrai-Szekeres, F. Fülöp, Spin Diffusion and Magnetic Eigenoscillations Confined to Single Molecular Layers in the Organic Conductors κ-$(BEDT\text{-}TTF)_2Cu[N(CN)2]X$, (X=Cl, Br), Phys. Rev. Lett. **102**, 086404 (2009)