ESR study of antiferromagnetic spin systems

PhD thesis booklet

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Budapest

2014

Background

I prepared my PhD thesis under the supervision of András Jánossy. My work deals with three topics: instrument development, and the investigation of magnetic properties of the high temperature superconductor material ($YBa_2Cu_3O_6$, YBCO) and an organic charge transfer ($ET_2MnCu[N(CN)_2]_4$) salt .

The high field electron spin resonance spectrometer, the main instrument of the research group, was built by András Jánossy and his students a decade before. I participated in the modernization of this instrument. In my research work I utilized the increased sensitivity and new probe heads of the refurbished apparatus.

High temperature superconductors have a layered structure. Two dimensional copper oxide planes are common to all such materials and unambiguously these structures are essential components for high temperature superconductivity. In stoichiometric composition, the conduction band of these materials is half full and the ground state is an antiferromagnetic Mott insulator.

Composition of the layers in between the copper-oxide planes is quite diverse within the material family. With chemical doping of these layers one can introduce charge carriers, typically holes to the copper-oxide planes. In the low doping region of high temperature superconductors, the holes introduced to the Mott insulator background undergo a cooperative segregation, forming an insulating ground state. The structures formed by the segregating holes are called “stripes”

YBCO has been studied in the research group for years. ESR spectrum of the undoped material was solved and they started the research of calcium doped samples. They discovered that the magnetic structure alters already at low doping as the sublattice magnetization rotates by 45°. This already happens at very low doping (0.8% Ca) suggesting that holes interact with the magnetic collectively, as a stripe.

The second part of my work deals with the charge transfer salt, $ET_2MnCu[N(CN)_2]_4$.

The first organic molecule-crystals exhibiting metallic behavior, were discovered in the 50’s. Most of the molecular metals are charge transfer salts, where donor molecules give partial charge to the acceptors and the resulting electrostatic interaction stabilizes the crystal. The donor molecule is typically TTF or one of its derivatives. These heterocyclic molecules form the conduction band. Overlap of the conduction band with the neighboring anions is generally weak and conduction properties are strongly anisotropic. Physical and chemical properties of the anions are not constrained, so basically any anion can be combined with the conductor.

A broad family of molecular conductors has the generic structure K_2X, where K is a donor molecule and X is the anion. These materials have quasi-two-dimensional structure where the anions and the cations form alternating layers. The electronic ground state, that can be insulator, metal or superconductor is fundamentally determined by the ordering of the cations within the layer.

The charge transfer salt I studied has a very unusual structure. We received it right after it was synthetized and apart from the basic characterization measurements it was not studied before.

Motivation

During the refurbishing of the SER spectrometer, we installed new microwave sources, a quasi-optical bridge and we developed a several new probe heads. The main goal was to improve the sensitivity of the system.

My scientific studies aimed at the better understanding of magnetic properties of antiferromagnetically correlated materials.

The understanding of high temperature superconductivity would have great scientific and economic significance. In the low doping region there are very high quality samples available to study the interaction of collective electron states.

I was probing the low doping range of $YB_2Cu_3O_6$ (YBCO) through a series of calcium doped single crystals. After characterization of the samples I studied the doping, temperature and magnetic field dependence of the charge segregated phase.

I also studied the interaction of the charge segregation and the antiferromagnetic order. It was observed before, that “stripes” can change the orientation of the magnetic order, so it is a valid question that by rotating the sublattice magnetization with an external magnetic field can one realign the coupled charge structures?

The material $ET_2MnCu[N(CN)_2]_4$, that I discuss in the second part of my thesis, has a very interesting structure. The anions form a three-dimensional network, which is quite unusual for organic charge transfer salts.

Theoretically, when combining different molecules in charge transfer salts their characteristic physical properties should also combine, forming “hybrid materials”. Using this concept materials with very unlikely physical properties were synthetized, like ferromagnetic superconductors. In “hybrid material” research probably the most effort was put into finding magnetic conductors. As conduction electrons of the cationic layer usually have very small overlap with the neighboring molecular layers, combining magnetic anions and conducting cationic layers generally does not result magnetic order.

My research was motivated by that interconnected anionic structures tend to enhance the coupling of the magnetic ions that increases the chance of magnetic ordering.

New results

1. I participated in the development of the high frequency electron resonance spectrometer at the BME Institute of Physics, Magnetic Resonance Lab. I was testing the instrument and I measured its sensitivity. I proved that its stability and noise level meet the design specifications. I designed and developed a probe head for the investigation of highly conducting liquid samples.[1]
2. I performed Gd^{3+} ESR experiments at 9 GHz on samples of the high temperature superconductor $Gd_yCa_xY_{1-x-y}Ba_2Cu_3O_6$ (YBCO) in the low doping, antiferromagnetic state. I determined the phase diagram of the “stripe” phase as a function of temperature and doping concentration.[2]
3. I determined with ESR in 2% Ca doped YBCO the magnetic field and temperature dependence of the sublattice magnetization M_S in the range of 0.8-8.1 Tesla and 3 – 100 K, respectively. I found that rotating M_S by 90° requires lower magnetic field than to stabilize it at 45° rotation.[2]

4. I studied the charge segregated phase of slightly doped high temperature superconductors in infrared transmission experiments using calcium doped YBCO samples. I showed that while the magnetic order can be realigned with external magnetic field, the charge structures cannot be reoriented. In light of my results the existence of strongly coupled charge and spin structures is unlikely in the charge segregated phase.[2]
5. I performed ESR measurements on the newly synthetized charge transfer salt $ET_2MnCu[N(CN)_2]_4$. In the environment of the manganese ions of the two dimensional layers I detected a tetragonal distortion along the c axis, within the planes, below 150 K. I quantified the distortion using second order crystal field parameters.[3]
6. I showed that the coupling between the different magnetic moments in $ET_2MnCu[N(CN)_2]_4$ is extreme anisotropic: It is several orders of magnitude stronger within the two-dimensional layers, then between them. Analyzing ESR spectra I estimated the coupling between manganese ions and ET molecules at 300 K: $|J_{Mn\text{-}ET}| \approx 4 \cdot 10^{-2}$ K, and I gave a lower estimate of the coupling between manganese ions at 100 K: $|J_{Mn\text{-}Mn}| \geq 48$ K.[3]

Publications connected to the results

1. **Multipurpose High-Frequency ESR Spectrometer for Condensed Matter Research**
   Kálmán L. Nagy, Dario Quintavalle, Titusz Fehér and András Jánossy
   Applied Magnetic Resonance, 40, 47-63, (2011), DOI: 10.1007/s00723-010-0182-4
2. **Search for Stripes in Lightly Hole Doped YBCO by ESR and IR Transmission**
   András Jánossy, Kálmán L. Nagy, Titusz Fehér, László Mihály and Andreas Erb
   Phys. Rev. B. 75, 024501 (2007)
3. **Multifrequency ESR in ET2MnCu[N(CN)2]4, a radical cation salt with quasi two dimensional magnetic layers in a three dimensional polymeric structure**
   K. L. Nagy, B. Náfrádi, N. D. Kushch, E. B. Yagubskii, E. Herdtweck, T. Fehér, L. F. Kiss, L. Forró, A. Jánossy
   Phys. Rev. B. 80, 104407 (2009)

Other publications

- **Performance Evaluation of the Small-Animal nanoScan PET/MRI System**
  Kálmán Nagy, Miklós Tóth, Péter Major, Gergely Patay, Győző Egri, Jenny Häggkvist, Andrea Varrone, Lars Farde, Christer Halldin, and Balázs Gulyás
  J. Nucl. Med. 54, 1825-1832 (2013), DOI: 10.2967/jnumed.112.119065
- **Two-magnon scattering and viscous Gilbert damping in ultrathin ferromagnets**
  K. Lenz, H. Wende, W. Kuch, K. Baberschke, K. Nagy, and A. Jánossy
  Phys. Rev. B 73, 144424 (2006)