

Polytech network form for PhD Research Grants from the China Scholarship Council

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PhD information	
Title	Structure, disorder and electron-phonon coupling in bi-dimensional kappa-(BEDT-TTF)₂X charge-transfer spin-liquids and multiferroics
Main topics regards to CSC list (3 topics at maximum)	Structural and electronic properties of materials

Required skills in science and engineering	Competences in condensed matter
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Subject description (two pages maximum)

This PHD will be in co-direction with V. Ilakovac, LPCM, University Pierre et Marie Curie.

Strongly correlated systems show a number of exotic phenomena, like superconductivity and magnetism, which cannot be understood without including many body interactions. Subtle balance of different factors: on-site correlation (U), exchange interaction (J), spin-charge or electron-phonon interaction, can result in complex phase diagrams with different ground states dependent on pressure or doping. The competition of different types of insulating and magnetic states with superconductivity is studied in organic conductors for decades [1]. The discovery of the quantum spin liquid ground state or the multiferroicity is more recent, but even more intriguing [2,3]. The first appears in materials with a strong magnetic frustration, where, despite strong antiferromagnetic coupling, quantum fluctuations prevent any spin ordering. The latter is characterized by the co-existence of a magnetic and a ferroelectric order, which is rather rare.

Bi-dimensional charge-transfer salts kappa-(BEDT-TTF) $_2$ X are particularly interesting as they can present all these properties, depending on the counter-anion (X), and external parameters, like pressure and temperature. Their structure is composed of layers of triangular constellation of dimers of BEDT-TTF (bis-(ethylene-thio)-tetra-thia-fulvalene) molecules, separated by anion layers parallel to the (b,c) plan. There is a charge transfer of about one electron per dimer, from the BEDT-TTF molecular layer (donor) to the anion layer (acceptor). Thus the sites of the triangular lattice of dimers are accommodated by approximately one hole carrying a spin-1/2. We will be particularly interested in three of them, kappa-(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Cl (shortly K-Cl), kappa-(BEDT-TTF) $_2$ Cu $_2$ (CN) $_3$ (K-Cu) and more recently synthesized kappa-(BEDT-TTF) $_2$ Ag $_2$ (CN) $_3$ (K-Ag). An extremely subtle competition between the spin frustration and coulomb interaction results in their different ground states.

K-Cl presents an antiferromagnetic order below 27 K, while K-Cu and K-Ag do not show any magnetic order at low temperature [4-6]. Moreover, signs of ferroelectricity are observed in K-Cu and K-Cl. They were interpreted by a creation of electric dipoles on dimers of BEDT-TTF molecules [7-10]. The competition between the spin and the charge order should be here a result of an interaction between dipoles and spins [7-13]. In K-Cl, the ferroelectric order is proposed to be a motor of the magnetic order [10]. The situation seems to be inverse compared to the transition metal multiferroics, where the magnetic order induces the ferroelectric order. Surprisingly, the presence of dipoles in K-Cl, K-Cu and K-Ag has not been experimentally evidenced up to now [14-16]. Thus the discussion of the origin of the ferroelectric, spin-liquid, and multiferroic behavior in kappa-(BEDT-TTF) $_2$ X systems is still under hot debate. It requires a complete revision of the results of their structure and dynamics [17].

The object of the proposed work is to arrive at a consistent interpretation of the spin-liquid versus multiferroic behavior in kappa-(BEDT-TTF) $_2$ X salts. Combined effects of the disorder, the electronic correlation and of the spin frustration will be examined as possible motors of the spin-liquid and multiferroic behaviors. Particular attention will be given to the interplay between the anionic plane and the cationic molecular (BEDT-TTF) layer. The two subsystems are connected via hydrogen bonds, realized between the ethylene side-group of the BEDT-TTF molecule, and the anionic-plane nitrogen of the cyanide CN group. Side ethylene groups, pointing to the N atoms in the anion layer, can take different conformations relative to the plane defined by the rest of the molecule. Moreover, in K-Cu and K-Ag, one third of anion plane N atoms is positionally disordered due to the orientational disorder of bridging CN groups. The geometrical and charge frustration resulting from the two disorders can result in a creation of globally non-polarized domains separated by domain walls. Excitations inside these domain walls can be responsible for the ferroelectric behavior.

Questions about the ferroelectric, spin-liquid, and multiferroic behavior in kappa-(BEDT-TTF) $_2$ X will

be addressed by studying the detailed structure and the elemental excitations of three kappa-(BEDT-TTF)₂X salts: K-Cu, K-Ag and K-Cl. Three experimental techniques will mainly be used: x-ray diffraction, x-ray absorption and resonant inelastic x-ray scattering (RIXS).

New x-ray diffraction results show that K-Cu presents lower symmetry than its conventional mean structure [18]. This points to the necessity of a systematic and extremely detailed study of the structure of other members of the family, particularly K-Ag and K-Cl. This through but extremely interesting work includes a complete refinement of the structures, taking into account effects of the disorder in the anion plane and in the molecular layer. Diffraction experiments will be performed first using the 4 circle diffractometer in the Laboratoire de Physique de Solides, University Paris-Saclay, Orsay, France. Further, in order to record very weak reflections associated with an eventual symmetry breaking, measurements will be performed using the 4 circle diffractometer of the high flux beam-line CRISTAL at the synchrotron SOLEIL, St. Aubin, France.

Recent N K edge x-ray absorption and RIXS measurements reveal the importance of the electron-phonon coupling related to the anion-plane phonon modes in kappa-(BEDT-TTF)₂Cu₂(CN)₃ [19]. Moreover, it shows that the phonon excitation of two distinct nitrogen sites differs because they are more or less coupled to the molecular layer. The study of the electron-phonon coupling will be extended to K-Ag and K-Cl compounds. N K-edge (400 eV) and C K-edge (285 eV) X-ray absorption and RIXS measurement will be performed at SEXTANTS beamline at the synchrotron SOLEIL. Its RIXS spectrometer, AERHA, is unique as it covers the widest energy range (50 - 1000 eV), while having one of the best resolving powers in the world. It permits to measure elemental excitations, like dd-excitations, charge transfer, collective magnetic and phonon excitations.

The interpretation of the experimental data will be supported by theoretical *ab-initio* state-of-the-art electronic structure calculations, as well as the calculations of the x-ray absorption (XAS) and RIXS spectra. RIXS calculations will be performed in Laboratoire de Chimie Physique – Matière et Rayonnement (LCP-MR), UPMC, Sorbonne University, Paris, while XAS calculations will be performed in collaboration with Institut Néel, Grenoble, France.

We are confident that the study of the detailed structure and of the coupling of the lattice and charge degrees of freedom will permit to gain better insight into the origins of the ferroelectric, spin-liquid, and multiferroic behavior in selected kappa-(BEDT-TTF)₂X salts.

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