Sorbonne Université/ China Scholarship Council program 2020

Thesis proposal

Title of the research project: **Structure and elemental excitations in multiferoïc organic and metal-organic frameworks**

Keywords: ferroelectricity, magnetism, organic charge transfer salts, hybrid perovskites

Joint supervision: yes (Pascale Foury-Leylekian, Laboratoire de Physique des Solides, Université Paris-Saclay)

Joint PhD (cotutelle): yes (name/surname) /no

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Subject description (2 pages max):

1) Study context

Even if the ferroelectricity and the magnetic order usually appear separately, there are rare compounds, known as multiferroïcs, where the spin and the charge ordering coexist, and sometimes induce each other [1]. The mechanism of their coexistence is one of major questions in today's materials science. In the case of large magnetoelectric coupling, important applications of these materials can be found in data storage domain, as they offer the possibility to control ferroelectric properties by magnetic fields and magnetism by electric fields [2]. Moreover, they are important for the development of sustainable energy sources, like solar cells, as they offer the possibility of efficient ferroelectric polarization-driven carrier separation [3].

2) Details of the proposal

Bi-dimensional charge-transfer salts kappa-(BEDT-TTF)$_2$X are model systems showing various states, depending on the counter-anion (X), and external parameters (pressure, 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*) plane (see Fig.1). An extremely subtle competition between the spin frustration and the coulomb interaction results in their different ground states. In particular, some of them are multiferroïc [4,5], others are quantum spin-liquids, showing no spin ordering despite a strong antiferromagnetic interaction [6,7]. At the same time, most of them show some type of charge ordering [5].

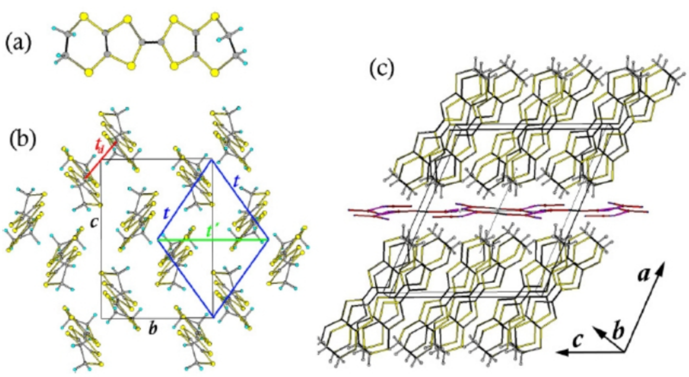

Figure 1 : Molecules BEDT-TTF (a) and their stacking along the **a** (b) and **b** (c) directions. The anion plane is shown in (c).

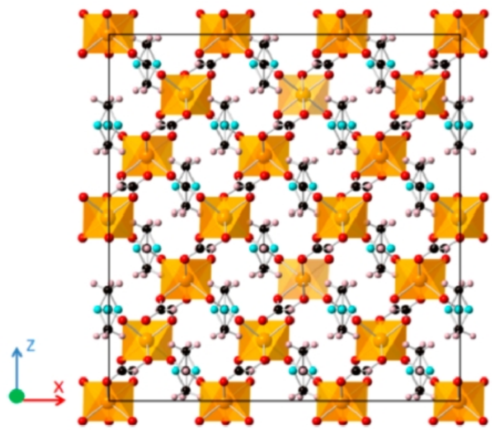

Figure 2 : Structure of the organo-metallic hybride perovskite [(CH)$_3$NH$_2$]Fe(HCOO)$_3$, showing Fe(HCOO)$_3^-$ skeleton and DMA [(CH3)NH2]$^+$ cations occupying the cavities.

On the other hand, in hybrid metal-organic frameworks with the AMX$_3$ perovskite-like structure the physical and chemical properties can be adjusted by varying components A and M. Besides potential applications in gas storage, catalysis, nonlinear optics, photoluminescence and solar cells, some of them are multiferroïcs with intriguing magnetoelectric properties. Here we will be particularly interested in the $[(CH)_3NH_2]Fe(HCOO)_3$ system, where the metal Fe^{2+} cation linked by formate groups ($X = HCOO^-$) form the FeX_2 skeleton and di-methyl-ammonium (DMA) cations ($A = [(CH3)NH2]^+$) occupy the cavities (see Fig.2), as it shows an intrinsic magnetoelectric effect at low temperature [8,9].

The object of the proposed work is to reach a better understanding of the conditions which are necessary to obtain a simultaneous appearance of the magnetic and the charge ordering. For this, we will study the detailed structure and the elemental excitations. Two experimental techniques will mainly be used: X-ray and neutron diffraction and Resonant Inelastic X-ray Scattering (RIXS). The interpretation of the experimental data will be supported by *theoretical ab-initio* state-of-the-art electronic structure calculations.

Description of the experimental techniques : *Resonant Inelastic X-ray Scattering (RIXS)* measures element resolved excitations, like dd-excitations, charge transfer, collective magnetic and phonon excitations [10]. Our goal is to probe modifications of these excitations related to the environment of the core-excited site [11]. X-ray absorption and RIXS measurement will be performed at SEXTANTS beamline at the synchrotron SOLEIL, St. Aubin, France. 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. The interpretation of the experimental data will be supported by simultations of the X-ray absorption and RIXS spectra. On the other hand, a detailed study of the structure will be done by *X-ray and neutron diffraction*, as recent results show that the conventional structure of these compounds is not always correct [12]. X-ray diffraction experiments will be performed first using a 4 circle diffractometer. Further, in order to record very weak atomic displacements associated with the electric polarization, measurements will performed on the high flux beam-line CRISTAL at the synchrotron SOLEIL. Moreover, in the multiferroic hybride perovskite $[(CH)_3NH_2]Fe(HCOO)_3$, it is important to investigate as well the magnetic structure which is expected to establish at low temperature. This will be performed in neutron facilities and in particular in ILL (Grenoble, France) or ISIS (United Kingdom).

3) References

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4°) Profile of the Applicant (skills/diploma…) Student with knowledge in chemical physics, material sciences or solid state physics. Good basis in crystallography and mater-light interaction is welcome.

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