CHINA SCHOLARSHIP COUNCIL

Appel à projets
Campagne 2022
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Title of the research project :

Structure and elemental excitations in multiferoïc metal-organic frameworks

Thesis supervisor (HDR) :

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Research Unit

Name : Laboratoire de Chimie Physique - Matière et Rayonnement
Code : UMR7614

Doctorate School Thesis supervisor's doctorate school (candidate's futur doctoral school) :
Chimie Physique et Chimie Analytique de Paris Centre, ED 388

PhD student currently supervised by the thesis supervisor (number, year of the first inscripton) : 0

Joint supervisor :

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Research Unit

Name : Laboratoire de Physique des Solides
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École doctorale

Joint supervisor's doctorate school : Physique en Ile de France, ED 564
Or, if non SU :
PhD student currently supervised by the joint supervisor (number, year of the first inscripBon) :

SORBONNE UNIVERSITÉ

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Structure and elemental excitations in multiferoïc metal-organic frameworks

Subject description:

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].

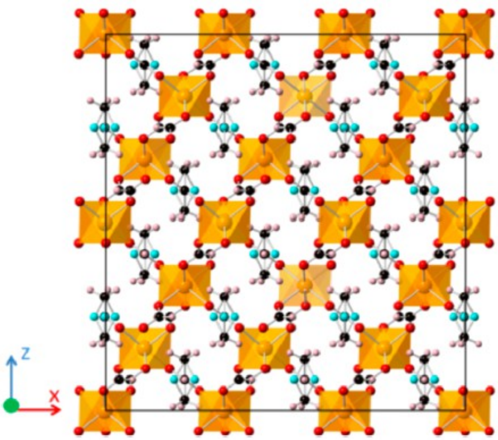

Fig.1 : Structure of the organo-metallic hybride perovskite $[(CH)_3NH_2]Fe(HCOO)_3$, showing $Fe(HCOO)_3^-$ skeleton and DMA $[(CH3)NH2]^+$ cations occupying the cavities.

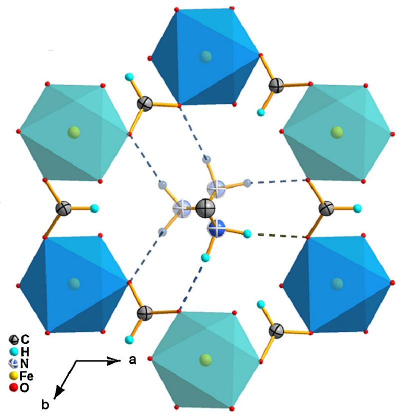

Fig.2 : ***Three possible orientations of the DMA cation inside a cavity., giving rise to a desorder at room temperature.***

2) Details of the proposal

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 $[(CH)_3NH_2]M(HCOO)_3$ family of systems. In their structure, the metal cation M = Fe^{2+}, Mn^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+} linked by formate groups (X = $HCOO^-$) form the MX_2 skeleton. The di-methyl-ammonium (DMA) cations (A = $[(CH3)NH2]^+$) occupy the cavities (Fig.1). ***They can orient in three different ways at room tempartune (Fig.2).*** The members of the family show an intrinsic magnetoelectric effect at low temperature [4,5,6]. 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.

Three 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.

Resonant Inelastic X-ray Scattering (RIXS) measures element resolved excitations, like dd-excitations, charge transfer, collective magnetic and phonon excitations [7]. Our goal is to probe modifications of these excitations related to the environment of the core-excited site [8]. 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.

This part of the thesis project will be directed by Vita Ilakovac, who has an expertise in resonant spectroscopy on various organic, inorganic and metallo-organic systems.

Detailed study of the structure will be done by *X-ray and neutron diffraction*, as recent results show that the conventional structure of complex compounds with organic component is not always correct [9,10]. *X-ray diffraction* experiments will be performed first using a 4 circle diffractometer in Laboratoire de Physique des Solides. 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. The magnetic structure investigation will be performed by *neutron diffraction* experiments in ILL (Grenoble, France) or ISIS (United Kingdom).

This part of the project will be carried out in the Pascale Foury-Leylekian's group, specialized in studies of the structure and physical properties of organic, inorganic and hybride multiferroïcs.

3) References

[1] S. W. Cheong and M. Mostovoy, Nat. Mater. **6** (2007) 13
[2] M. Gajek et al., Nat. Mater., **6** (2007) 296
[3] R. Nechache et al., Nat. Photon., **9** (2015) 61
[4] G.P. Nagabhushana, et al., J. Am. Chem. Soc., **137** (2016) 10351.
[5] Wang, W. et al., Sci. Rep. **3** (2013) 2024
[6] Y. Tian, et al., J. Am. Chem. Soc. **138** (2016) 782
[7] L. Ament et al., Rev. Mod. Phys. **83** (2011) 705
[8] V. Ilakovac et al., Phys. Rev. B **96** (2017) 184303
[9] P. Foury-Leylekian et al, Crystals **8** (2018) 158
[10] P. Foury-Leylekian et al, Acta Cryst. B **76** (2020) 581

4) Profile of the Applicant

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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