Temperature and doping effects on the electronic structure of solids : theory and experiment

The goal of this thesis is to study the modification of the environement of particular elements (N, Cu, C, O) in solids with strong electron correlations. The environement of an element can change either due to a structural change, related to a phase transition, or can be inherent and variable by the effect of doping (substutution of an element par another). The first system we plan to study is TTF-TCNQ, which exhibits a Peierls instability in TCNQ chains, and becomes insulating at low temperature. As the TCNQ molecule contains four cyano groups, we will focus on the nitrogen enviroment change across this phase transition. In the family of spin-chains and ladders, $(La,Y)_y(Sr,Ca)_{14-y}Cu_{24}O_{41}$, the pattern of copper-oxygen squares is different in chains and ladders. We will thus be interested in the copper valence in these two sub-systems.
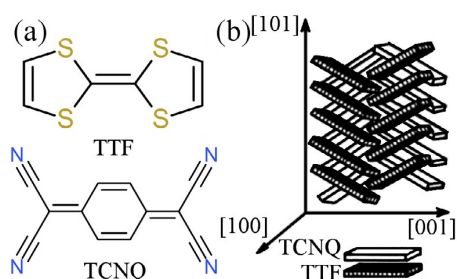

Fig.1 : TTF and TCNQ molecules (a). Schematic presentation of their stacking in TTF-TCNQ (b).
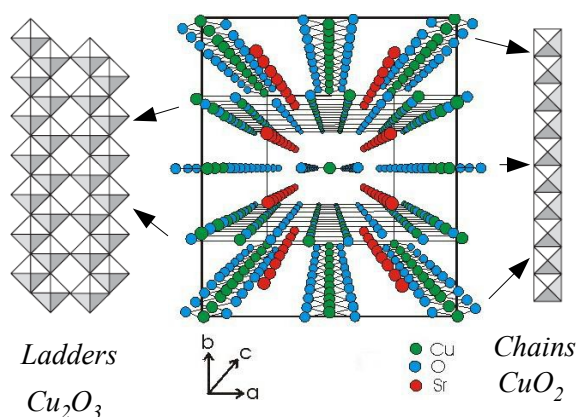

Fig.2 : Structure of $Sr_{14}Cu_{24}O_{41}$, constituted of ladders (left) and chains (right).

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Skills : Student with good background in solid state physics or chemistry, wishing to perform simulations of inner shell excitation spectra, and to participate to synchrotron radiation experiments.

Background :

The first quasi-one-dimensional charge transfer salt, TTF-TCNQ, is composed of stacks of TCNQ (7,7,8,8-tetracyano-p-quinodimethane) and TTF (tetra-thia-fulvalene) molecules, as presented in Fig.1. Its metallic properties are due to a charge transfer of ρ = 0.55 electrons from the HOMO (highest occupied molecular orbital) of the TTF to the LUMO (lowest unoccupied molecular orbital) band of the TCNQ. It exhibits three successive $2k_F$ Peierls transitions, progressively destroying its metallic character [1]. The first one, at 54 K, happens in the TCNQ stacks, where the charge density wave modulation opens a gap in the LUMO band, the second in the TTF stacks, below 49 K. The third one at 38 K, involves the two sub-systems, and increases the TTF → TCNQ charge transfer to ρ = 0.59 electrons, as well as an out-of-plane deformation of the TCNQ molecule [3].

As the TCNQ molecule contans 4 cyano groups, in this system we plan to study the modifications of the nitrogen environment when lowering the temperature, by measuring its charge transfer and vibrational excitations which can be revealed by N K-edge resonant inelastic x-ray scattering (RIXS).

The family $(La,Y)_y(Sr,Ca)_{14-y}Cu_{24}O_{41}$, became famous when the superconductivity is discovered in one of its members ($Sr_{0.6}Ca_{13.6}Cu_{24}O_{41}$) [4,5]. Their structure contains alternating layers of CuO_2-chains and Cu_2O_3-ladders, see Fig.2, separated by La/Y/Sr/Ca atoms. They are intrinsically hole-doped materials. For the parent $Sr_{14}Cu_{24}O_{41}$ system or for isovalently substituted $Sr_{(14-x)}Ca_xCu_{24}O_{41}$, the stoichiometry implies an average copper valence of +2.25, or 6 holes per formula unit. When the divalent Sr/Ca atoms are substituted by trivalent La/Y, the number of holes decreases. But the distribution of holes between chains and ladders is still a controversy. When the number of holes is progressively increased from *n=0* (in $La_6Ca_8Cu_{24}O_{41}$) to *n=6* (in $Sr_{14}Cu_{24}O_{41}$), the holes start to accommodate first on chains. From a certain number n_c, not yet exactly known, a part of holes is transferred to ladders [6]. For the $Sr_{14}Cu_{24}O_{41}$ system, polarization dependent absorption measurements at the O K edge show that at room temperature 5 holes reside on chains and one on ladders [7]. The question is important because the distribution of holes is closely related to the number of charge carriers in ladders, which are Zhang-Rice singlets, like in high T_c cuprates.

In the $(La,Y)_y(Sr,Ca)_{14-y}Cu_{24}O_{41}$ familly, we will be interested in the valence of the copper in chains and ladders, pointing to the ammount of holes they contain, which can be measured by the (resonant) photoemission at the Cu L edge.

Methods :

Core-level spectroscopies are particularly adapted for this study, as they are sensible to the local environment of the excited atom, which can vary from site to site. The progress of sources with variable energy, and the spectrometers with high resolving power, permitted their rapid developpement. This experimental improvement is accompanied and even motivated by an extraordinary developpement of the theoretical description of the inner shell excitation processes, permitting detailed interpretation of the spectra. LCPMR is one of laboratories with the expertise in the theory of the core-level spectroscopies, currently developping the description of the Cu L edge excitation. At the same time it has the state-of-the-art experimental knowledge in this domain.

For this study we plan to perform NEXAFS (near edge x-ray absorption fine structure), XPS (x-ray photoemission spectroscopy) and RIXS (resonant inelastic x-ray scattering) mesurements. While NEXAFS and XPS probe, respectively, unoccupied and occupied states of the excited element, RIXS probes both. The spectra will be interpreted by theoretical calculations using commercial codes, and as well codes developed in LCPMR, in order to describe in a simultanous way the electronic part, for example, the spin-orbit coupling, and the vibrationnal part of the excitation process.

[1] J.P. Pouget, *Highly Conducting Quasi-One-Dimensional Organic Crystals, Semiconductors and Semimetals* (Academic Press, New York, 1988), Vol. **27,** Chap. 3, pp. 87–214

[2] A. Chernenkaya et al, Eur. Phys. J. B **88** (2015) 13

[3] Y. Bouveret, S. Megtert, J. Phys. France **50**, 1649 (1989)

[4] M. Uehara et al., J. Phys. Soc. Jpn. **65** (1996) 2764

[5] T. Vuletic et al., Phys. Rep. **428** (2006) 169

[6] T. Ivek et al., Phys. Rev. B **78** (2008) 205105

[7] N. Nücker et al., Phys. Rev. B **62** (2000) 14384