

NEUTRAL-TO-IONIC PHASE TRANSITION UNDER PRESSURE:  
TOWARDS THE QUANTUM LIMIT

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One of the most fascinating features of molecular materials, is the possibility to tune in a co-operative way the state (valence, spin...) of the molecules under the effect of pressure, temperature or with light. The transfer of electron is fundamental to many chemical and biological processes in nature, but in solids, it may be highly efficient because of the intrinsic co-operativity of the organized condensed matter. Beside many insulating solids where an excited electron induces a local structural distortion, in some unconventional materials the relaxation of excited states results in drastic structural changes involving a large number of atoms and electrons [1]. TTF-CA is a prototype for such co-operative phenomena, as it exhibits the so-called neutral-ionic (N-I) transition where the electronic and structural aspects are strongly coupled [2]. This transition occurs in some quasi-one-dimensional charge transfer (CT) organic crystals with a mixed stack architecture (alternation of electron donor (D) and electron acceptor (A) molecules along chains). The electron transfer is intermolecular, mostly along the chain, and gives rise to a change of molecular ionicity, i.e. the degree of CT, associated with a dimerization process leading to the formation of (D<sup>+</sup>A<sup>-</sup>) pairs along the stack in the I phase. With regards to the regular N chains, the dimerization distortion for the I chains is associated with the inversion centre loss with two possible degenerated ferroelectric states (Fig 1). At finite temperature, localized CT exciton-strings, made of hundreds of adjacent (D<sup>+</sup>A<sup>-</sup>) excited pairs along the stack [3] may be thermally induced:



Specific to low-dimensional systems where electron-phonon couplings are important, these

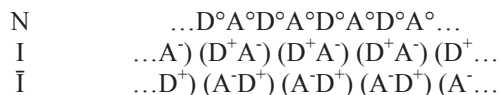


Figure 1. N and I (degenerated) states of a stack.

non-linear excitations can be discussed in term of self-trapped excitons which can self-multiply, and governed numbers of intriguing physical properties: photo-induced transformation [4,5], giant dielectric response ... In these insulators, the co-operative effects may expand to extreme, on contrary to classical insulator like NaCl where excitonic processes remain local. For the prototype complex TTF-CA, the thermodynamics of the N-I transition can be described in terms of three dimensional condensation of these non-linear CT excitations and there simultaneous or successive ordering, with a profound analogy with the solid-liquid-gas phase diagram [6]. Three phases are identified in the (P,T) phase diagram: the N<sub>para</sub> paraelectric phase, dominantly N with a low concentration in I fluctuating CT strings, the I<sub>para</sub> one, with a high concentration in I fluctuating CT strings, while the third I<sub>ferro</sub> phase is characterized by a ferroelectric ordering between I strings.

Since its discovery, most of the efforts to understand the mechanism of the transition were focussed on the finite temperature transition and plenty of its unusual physical changes are now well understood in terms of thermal activation mechanisms [5,7]. However fundamental questions such as the universality of the solid-liquid-gas phase diagram for the N-I transition or the crossover from thermal to quantum mechanism responsible of the N-I transition when it goes to take place in the ground state, remain and the (BEDT-TTF)-(ClMeTCNQ) [8] complex appears as a good guinea pig among the family of mixed-stack CT compounds. In that compound electrical resistivity and spectroscopy measurements have evidence a N-I transition, similar to that of TTF-CA, which should go down to zero Kelvin under pressure [8]. Therefore we have taken advantage of the new high pressure facilities developed at LLB (Helium pressure cell up to 650 MPa), combined with ILL ones (either with the classical He pressure cell or the new TiZr liquid one) to

investigate the structural aspects related to this phase transition, going down to zero Kelvin. Helium presents the priceless advantage to remain fluid over a very wide range of pressure and temperature, assuring a perfectly hydrostatic and controlled pressure on the samples, a control of external conditions which is essential for molecular crystals. From the symmetry point of view, the neutron analysis combined with a new X-ray measurement, has revealed that, on contrary to the literature which gives a  $P2_1/n$  space group alike TTF-CA, the diffraction pattern is characteristic of a  $P2_1$  space group, with a clear  $(0k0)$ :  $k=2n+1$  systematic absence, related to the twofold screw axis. (reflexions with indices  $(h0l)$ :  $h+l=2n+1$  are clearly present in the diffraction pattern and their width is always characteristic of long range order). It is the first time that a neutral phase corresponds to a  $P2_1$  non-centrosymmetric space group. It means that the dimerization already exists between D and A molecules in the neutral state, where the ionicity of molecules is weak ( $\rho \sim 0.3$ ). In order to understand this unexpected phenomena of dimerization in the neutral state, a complete analysis of the structure is presently in progress, taking into account the combination of the effects

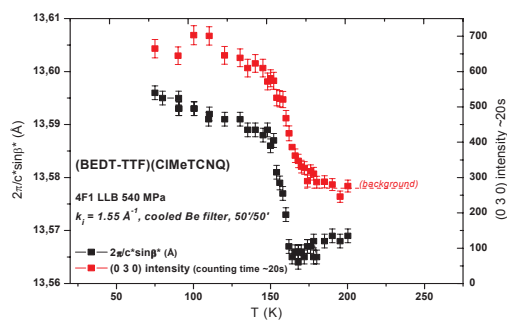


Figure 2. (BEDT-TTF)-(ClMeTCNQ) c cell parameter and intensity of  $(030)$  Bragg peak versus temperature at different pressures.

due to Madelung interactions and to the electrical field due to the non-centrosymmetry of the ClMeTCNQ molecule. Under pressure at low temperature, we have evidenced, thanks to neutron diffraction experiments (4F1 at LLB and D10 at ILL), that the transition is related to the appearance of  $(0k0)$ :  $k=2n+1$  Bragg peaks, characteristic of the symmetry breaking, and to clear unit-cell parameter anomalies (Fig. 2). The transition is therefore associated to a  $P2_1 \rightarrow P1$  change of symmetry and it goes down to absolute zero under a moderate pressure of  $\sim 200$  MPa. On contrary to TTF-CA, only the symmetry breaking transition is observed, becoming more and more first order as pressure increases, with phase coexistence phenomena (as testify by the enhancement of Bragg peak width when crossing the transition), and with a very strong sample dependence of the low temperature limit of metastability. (BEDT-TTF)-(ClMeTCNQ) appears as a rather more complex case of N-I transition than TTF-CA but gives also the opportunity to investigate the related phenomena in a more rich case up to the quantum regime and including localized field effects.

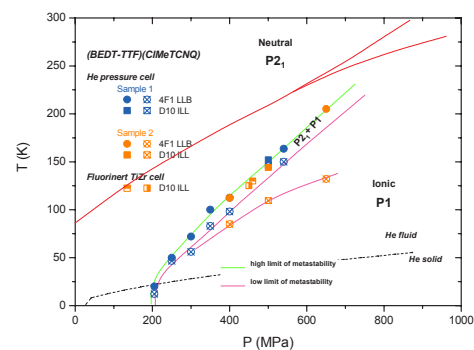


Figure 3.  $(P,T)$  phase diagram of (BEDT-TTF)(ClMeTCNQ). One can clearly see the difference of low temperature metastability limit according to sample, while the high temperature limit is weakly affected. The red lines give the TTF-CA diagram.

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