ESRF	**Experiment title:** **CHARGE-TRANSFER MULTI-EXCITON STRINGS AT THE NEUTRAL-TO-IONIC TRANSITION**	**Experiment number**: 02 02 151
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The possibility to tune between different ground states is one of the most fascinating features of some organic materials. This situation especially occurs in some quasi-one-dimensional charge-transfer (CT) complexes with mixed-stack architecture, where the alternation of electron donor (D) and acceptor (A) molecules gives rise to chain multistability between a regular neutral (N) state …D°A°D°A°D°A°… and two degenerate dimerized ionic I_+ …$(D^+A^-)(D^+A^-)(D^+A^-)$… and I_- …$(A^-D^+)(A^-D^+)(A^-D^+)$… states. Electronic and structural aspects are especially closely coupled : changes of the electronic state only exist with large structural distortions, affecting both intra- and inter-molecular geometry. The thermal activation of lattice-relaxed CT exciton-strings is at the heart of N-I transition mechanism:

...D°A°D°A°**$(D^+A^-)(D^+A^-)(D^+A^-)$**D°A°D°A°...

This type of non-linear excitations, specific of quasi-one-dimensional systems with strong electron-phonon coupling, can also be discussed in terms of self-trapped CT multi-excitons, called CT strings. Many intriguing physical properties are governed by these non-linear excitations. At finite temperature the thermal excitation of boundaries between “phases” destroys any long range order and the isolated chain becomes intrinsically inhomogeneous with the condensation of structurally relaxed CT strings. Inter-chain coupling in the crystal can drive phase transitions [1], and thus the so-called N-I transition may be induced by temperature, pressure and also light. Crystalline inter-chain organisations may lead to different ordering schemes. In the prototype compound, tetrathiafulvalene-chloranil (TTF-CA), a singular solid-liquid-gas like (P,T) phase diagram [2] associated with the

condensation of CT strings which can next order (crystallize) with a ferroelectric arrangement between dimerized ionic chains [3].

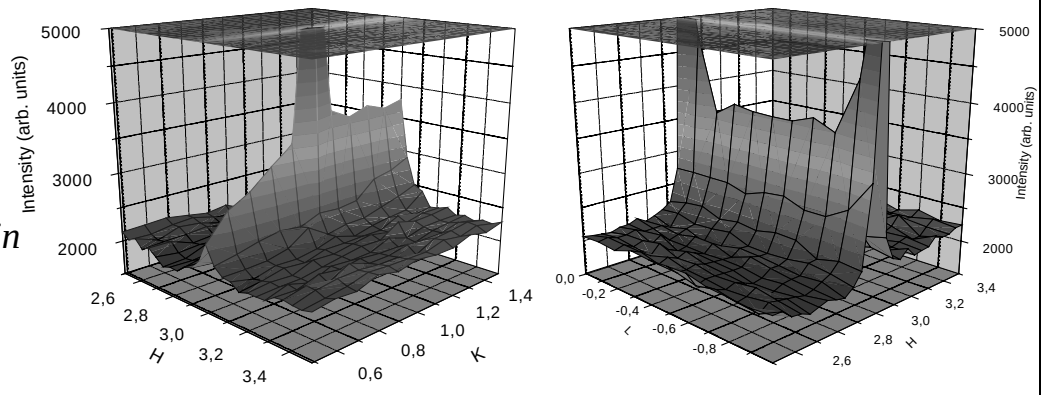
N_{para} (gas-like phase)	I_{para} (liquid-like phase)	I_{ferro} (solid-like phase)
... D° A° D° A° D° A° D° A° ...	... (D^+A^-) (D^+A^-) D° A° D° A° ...	... (D^+A^-) (D^+A^-) (D^+A^-) (D^+A^-) ...
... (D^+A^-) (D^+A^-) D° A° D° A° ...	... D° A° (D^+A^-) (D^+A^-) (D^+A^-) ...	... (D^+A^-) (D^+A^-) (D^+A^-) (D^+A^-) ...
... D° A° D° A° D° A° D° A° ...	... D° (A^-D^+) (A^-D^+) A° (D^+A^-) ...	... (D^+A^-) (D^+A^-) (D^+A^-) (D^+A^-) ...

We have recently evidenced such type of charge-transfer excitations in a derivative of TTF-CA, 2,6-dimethylTTF-CA (DMTTF-CA) [4], with high- and low-resolution studies performed on D2AM (Oct 00), and at Orsay. It was clearly established that :

- down to T_c+10K, well defined diffuse planes were observed, characteristic of 1D CT strings.
- between T_c and T_c+10K, precursor 3D ordering took place with very large anisotropy between inter- and intra-stack correlation lengths ($\xi_{intra\text{-}chain} \sim 10\ \xi_{inter\text{-}chain}$).

In this experiment, we have observed structural evidences of the condensed CT excitations on the prototype compound TTF-CA : diffuse planes have been evidenced above the phase transition (@82K) up to 200 K (Figure 1). The temperature behaviour is similar for both TTF-CA and DMTTF-CA and the typical size for the CT-string increases here from about 20 Å at 200 K to about 50 Å just above $T_{N\text{-}I}$.

Figure 1: Diffuse (b,c*) planes associated with the 1D nature of the charge-transfer exciton-strings in TTF-CA.*



But contrary to DMTTF-CA [4], no precursor behaviour is observed for the ordering of the CT exciton-strings on the inter-chain correlation lengths, the transition beeing strongly first order. Below the transition, weak diffuse scattering is also observed with no evolution of the shape and intensity in temperature. It may origin from pinned polarons appearing when I_+ and I_- domains form at $T_{N\text{-}I}$: **...$(D^+A^-)(D^+A^-)D^0(A^-D^+)(A^-D^+)(A^-D^+)A^0(D^+A^-)(D^+A^-)(D^+A^-)$...**
The analysis of dipolar and quadrupolar contribution to this diffuse scattering has not been possible (instability of the cryogenic system for peculiar diffraction geometry) and requires other investigations in a near future.

[1] Cailleau et al, in NATO advanced series "Frontiers of high pressure research : application of high pressure to low dimensional novel electronic materials", Eds H.D. Hochheimer, B. Kuchta, Nato conference (2001).

[2] Lemée-Cailleau et al, Phys. Rev. Lett. 79, 1690 (1997).

[3] Le Cointe et al, Phys. Rev. B 51, 3374 (1995).**[4]** E. Collet et al, submitted Europhysics Letters