NEUTRAL-IONIC TRANSITIONS AS THE CONDENSATION AND ORDERING OF CHARGE-TRANSFER EXCITON-STRINGS.

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Many novel low-dimensional electronic materials, organic and inorganic, exhibit a high tunability between competing ground states. Interactions between charge, spin and lattice degrees of freedom are enhanced in the low-dimensional systems and cause cooperative phenomena and broken symmetries. The structure-function relationships are thus determined by self-trapped non-linear excitations, which induce intrinsic multiscale spatial structures and associate multiple timescales. Besides well-known examples such as high-Tc superconductors, manganite oxide perovskites, conducting polymers or mixed-valence chains, the mixed-stack charge-transfer (CT) organic compounds appear as other promising materials, in particular with the possibility of a neutral-ionic (N-I) transition, and can serve as model systems to study the physics of non-linear excitations. In those quasi one-dimensional systems, the alternation of electron donor (*D*) and acceptor (*A*) molecules along stacks (Fig. 1) gives rise to chain multistability between a regular neutral (N) state ...D^0 A^0 D^0 A^0... and two degenerate dimerized polar ionic (I_+ and I) states ...$(D^+A^-)(D^+A^-)$... and ...(A^-D^+) (A^-D+)... Compared with the N state, different intra- and inter-molecular structural distortions take place in the I states and the loss of inversion symmetry leads to the formation of ferroelectric chains. This unusual electronic-structural transition may be induced by temperature and pressure and is governed by the formation of lattice-relaxed (LR) CT exciton-strings, sequences of I dimers within N chains, ... D^0 A^0 $D^+A^-)(D^+A^-)$ D^0 A^0... [1], only recently directly evidenced by diffuse scattering [2].

New physical properties originate from these non-linear excitations, such as photo-induced phase transformations [3], new type of ferroelectric phenomena [4] or negative resistance effects [5]. The N-I transition may be analysed as a cascade of cooperative phenomena\,: formation of CT strings, their one-dimensional (1D) lattice relaxation which can be followed by their three-dimensional (3D) condensation and ordering, as it is the case in the singular (*P*,*T*) phase diagram of the prototype compound TTF-CA, similar to the solid-liquid-gas one [6] (Fig. 2). It was evidenced by different techniques with He pressure cells environment and especially the neutron scattering one available at LLB. The phase diagram can be described with two order parameters : the concentration *c* in *I* species (D^+A^-) (analogous to the density for the liquid-gas transition) and the symmetry breaking order parameter η (associated with the ferroelectric ordering between the dimerized *I* species). The first phase is the *N* one (N_{para}) with a low concentration in fluctuating *I* LR-CT excitations so that it is a disordered high symmetry phase ($c < 0.5$, $\eta = 0$). There is another disordered high symmetry phase which is the *I* paraelectric one (I_{para}) with a high concentration of I fluctuating excitations ($c > 0.5$, $\eta = 0$).

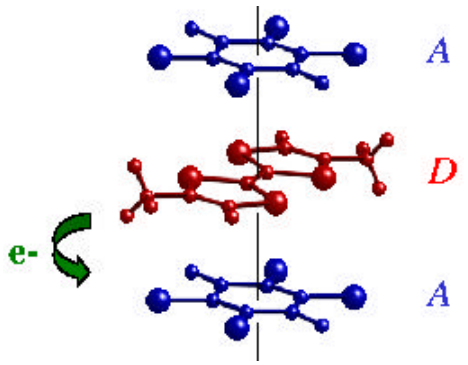

Figure 1. The mixed stack structure (here DMTTF-CA)

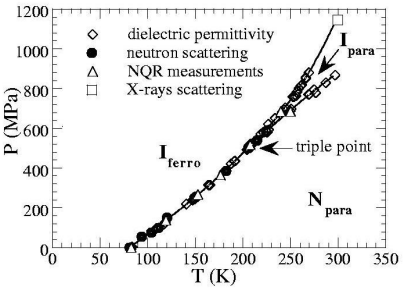

Figure 2 Phase diagram of TTF-CA described with gas-like CT excitation phase (N_{para}), a liquid-like one (I_{para}) and an ordered one (I_{ferro})

Between these two phases is the condensation line above the triple point, characterized by a discontinuous change of *c*, ending at a critical point. The last phase is the *I* ferroelectric one (I_{ferro}) with a ferroelectric ordering of the dimerized DA pairs ($c \approx 1$, $\eta \neq 0$). Above the triple point, located around 500 MPa, anomalies on the lattice parameters are observed for both the condensation and the crystallisation transitions [7]. The ferroelectric order associated with the last one is also characterized by the appearence of (0 2k+1 0) Bragg peaks.

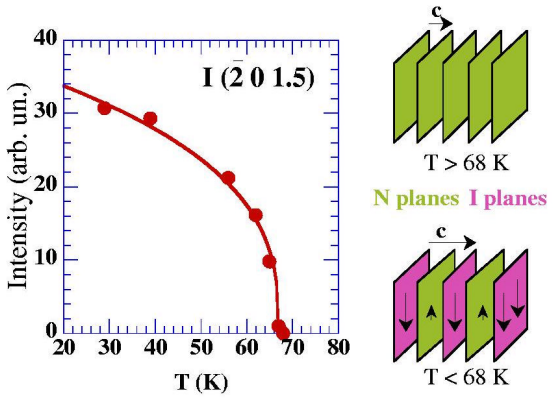

Figure 3. Cell doubling along c in DMTTF-CA, observed at $(\bar{2}01.5)$, associated with the N/I layering of the lattice. Below 68 K, both the stacks inside N and I planes are dimerized.

From one compound to another, different behaviours are observed. For example, we have recently reported that the DMTTF-CA compound undergoes a N-I transition of an unusual type, associated with a N/I ferrielectric layering of the lattice [8] below $T_c \cong 68$ *K*, with the regular alternation of antiparallel dimerized N and I (**a**,**b**) planes (**a** is the stacking axis). As characteristics for the transition, there are charge ordering and dimerization ordering. The transition between the N and N/I layered phases is then characterized by the appearance of superlattice reflections at **c***/2, as observed by neutron scattering measurements (Fig. 3).

A new mixed-stack CT compound, (BEDT-TTF)(ClMeTCNQ), has recently been synthesized [9]. The use of larger molecules than in the case of TTF-CA is supposed to suppress dimerization processes by an increase of inter-stack interactions, and so to induce the formation of paramagnetic I species. At high pressure, an I state is reached as it was observed by optical studies and electric measurements. The magnetic response observed by RPE increases with pressure on approaching the transition and no sign of dimerization is observed with IR spectroscopy. Recently a high resolution neutron diffraction experiment at constant pressure (400 and 540 MPa) on the triple axis spectrometer 4F1 at LLB has revealed clear anomalies on unit-cell parameters at the transition (Fig. 4), where a coexistence of the N and I phases is associated with the first order nature of the transition. The study of the symmetry breaking is now under investigations. One of the most interesting features of this compound is that it undergoes the N-I transition at 0 K under the only effect of pressure. Therefore it may be the good candidate to investigate quantum fluctuations at low temperature.

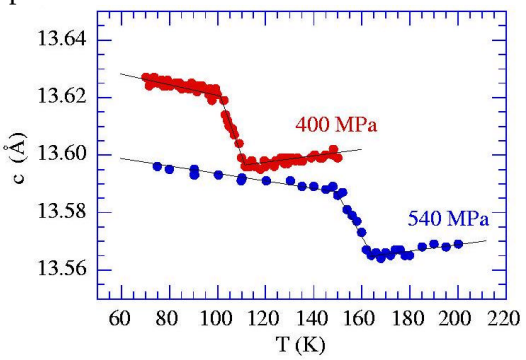

Figure 4. Jump of the lattice parameter c vs temperature at 540 and 400 MPa observed in (BEDT-TTF)(ClMeTCNQ).}

The N-I transformation in quasi-one-dimensional CT solids is an example of extreme electronic and structural cooperativity in molecular organic materials, where one can trigger under the effect of pressure and/or temperature the size, but also the concentration of electronic excitations, and so the physical properties. It may serve as model for thermo- and photo-chromic transformations in solids where cooperativity plays an important role. The existence of fast photo-induced transformations in this systems opens up the prospect of new applications.

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