ESRF	**Experiment title:** **TIME-RESOLVED DIFFUSE SCATTERING INVESTIGATION OF THE MECHANISM OF THE PHOTO-INDUCED NEUTRAL-IONIC PHASE TRANSITION IN TTF-CA**	**Experiment number**: CH-1904
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Report:

By virtue of cooperative photo-switching of molecular state (charge, spin …), the physical properties of materials can be manipulated in an ultra-fast way. The situation is carried to extreme when these photo-induced cooperative phenomena trigger a complete solid-to-solid phase transformation (photo-induced phase transition), leading to a light driven switching between different macroscopic states of the material with different physical properties: optical, dielectric, magnetic, conductivity…The structural relaxation of the molecular excited state following the absorption of photons is not made of independent processes, as conventional photochemical ones, but entails the transformation towards a new lattice structure and electronic order. This is exemplified in some charge transfer (CT) insulating molecular materials of mixed stack architecture that are readily tuned between neutral (N) and ionic (I) states (T_{N-I}~81K). It gives rise to a chain multistability between regular N state …D°A°D°A°D°A°… and two degenerate and polar dimerized I states …$(D^+A^-)(D^+A^-)(D^+A^-)$… and …$D^+)(A^-D^+)(A^-D^+)(A^-$… Structural and electronic changes are strongly coupled, as in the prototype compound tetrathiafulvalene-*p*-chloranil (TTF-CA), where a long range ferroelectric ordering of the dimers takes place in the I phase stable at low temperature [1].

In such materials, photoinduced transformation from I to N as well as from N to I molecular state has been evidenced by pump-probe optical reflection spectroscopy (change of color)[2], and then investigated by time-resolved x-ray diffraction at the ID09B beamline [3-6]. Collective structural rearrangements have been evidenced after laser irradiation of the N phase, generating the I one. An important feature is the observation in the diffraction patterns of a symmetry lowering in the photo-induced state establishing that a self-organized long-range ferroelectric order takes place [3]. The investigation of the I-to-N transformation (below T_{N-I}) by using the new helium flow cryostat was more recently performed. A two-step mechanism has been observed [4] as expected from optical measurements [7]: disappearance of the ferroelectric order (disordering process) before the I-to-N molecular transformation triggering the change in the intensities of Bragg peaks after 500 ps.

The recent improvements on ID09B will make it possible to go further in the investigation of the mechanisms associated with this transformation, via the study of short range order (diffuse scattering). Indeed, the structural relaxation of an optical CT excitation is not localized on one site, but yields the formation of a one dimensional nanodomain. Such lattice-relaxed CT excitations are at the heart of N-I transition mechanism, as observed at thermal equilibrium [9]:

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

When a large enough number of nanodomains is simultaneously created, subsequently to an ultrashort laser pulse, the interchain cooperativity leads to a switching towards a new macroscopic state. It manifests by the formation of three dimensional domains of the transformed phase. It is the goal of this experiment to evidence by diffuse scattering the formation of these 1D CT strings and to follow the transformation from the isolated molecules to the macroscopic 3D state, as successfully done at the ESRF at thermal equilibrium [9]. The diffuse planes associated with the 1D strings in the intermediate phase should disappear when the 3D order takes place. Therefore, the most important diffuse scattering signal is expected before the intensity of general Bragg peaks change, that is between 0 and 400 ps after the laser excitation starting from the high temperature N phase (Fig. 1).

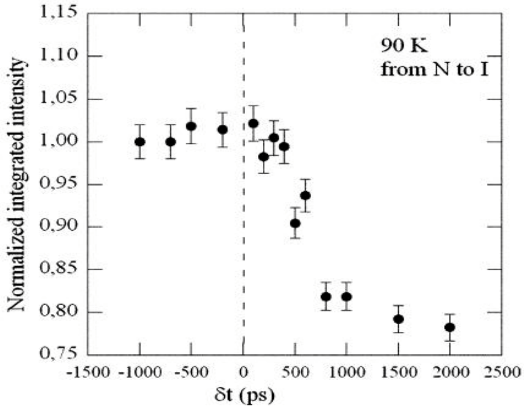

Fig. 1 : Normalized intensity of the 067 Bragg peak versus the delay between the laser pump and X-ray probe pulses. The important change of the intensity after a few 100 ps signs the structural reorganization in the photo-induced I phase. From [4]

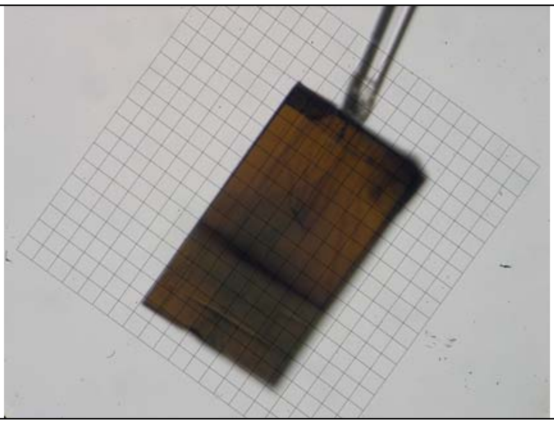

*Fig. 2 : The optimum shape for a crystal of TTF-CA is a very thin layer as 500*800*30 μm*^{3}

A diffuse scattering signal is always very weak in comparison to general Bragg peaks (typically five order of magnitude lower than strongest Bragg reflections in TTF-CA) [9]. Because a new multilayer was not available during the allocated beam time, we have worked on different crystals with the new objectives to reproduce the three-dimensional photo-induced phase transition, i.e. to observe the drastic change on intensity of general Bragg peaks as on Fig. 1 and to carefully look at a possible change on the volume of the unit-cell. We would like to underline that we spent a lot of time developing software and we can now treat online the complete data obtained for monochromatic diffraction on single crystal in different experimental conditions (laser power, single or double excitation of the crystal, i.e. light coming on both sides of the crystal, …). In other words, we can now know if the experimental conditions used are successful simultaneously to the data collection.

Although the crystals came from different sources (Rennes and Japan, growth in solution or by co-sublimation method), we could not observe the change on Bragg peak intensities as in Fig. 1, although such three-dimensional photo-induced phase transition has been observed during three different experiments on ID09 as well as once in Japan on the PF-AR NW 14 beam line in Tsukuba. The reasons of such a discrepancy become clear at present : the switching depends on the crystal (thickness, age, storage conditions, …). First, the use of a very thin crystal is essential in order to fully transform the crystal or at least to maximize the part of the photo-transformed region. Indeed the penetration depth of the light is limited to a few μm and the X-ray probe the whole crystal, i.e. the photo-transformed region and the stable one. Second, by using "old" crystals, we have observed for the first time a strong heating of the crystal (about 30 K) during this experiment on ID09, visible both on the Debye-Waller factors and on the lattice parameters, whereas just grown crystals break for the same excitation density. Besides, last march using a just grown and very thin TTF-CA crystal (Fig. 2) on the japanese beam line, a strong photo-induced signal has been observed without any laser heating effect. Our present control of the crystal synthesis will make it possible to realize future experiments in the best conditions.

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