ESRF	**Experiment title: Time-resolved X-ray diffraction investigation of ultra-fast photo-induced insulating-to-metal phase transition in a family of charge-transfe...**	**Experiment number**: CH-1741
Beamline: ID9B	**Date of experiment**: from: 15/12/2004 to: 20/12/2004	**Date of report**: 21/04/2006
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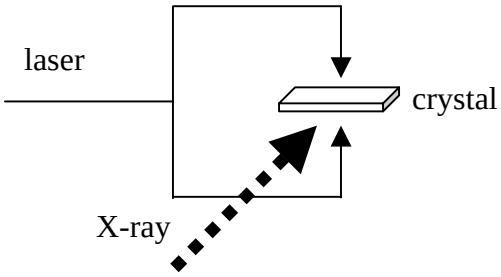
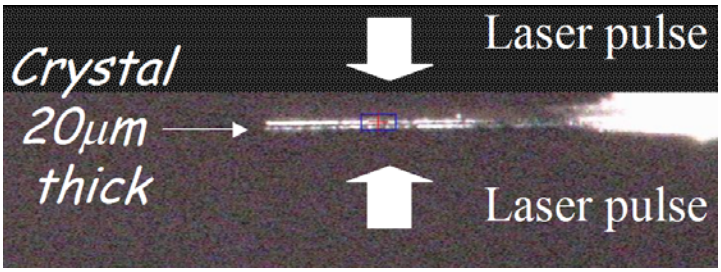
Report:

The photo-control of physical properties of a material (optical, magnetic, conduction, …) represents a fascinating research field. In previous experiments, we focused on the time-resolved X-ray study of the photo-induced N-to-I transition in the charge-transfer material TTF-CA [1,2]. During this experiment, we investigated the photoinduced phase transition of organic $(EDO\text{-}TTF)_2PF_6$ molecular conductor, which shows a photoinduced insulator (I) to metal (M) phase transition [3], which looks similar to the thermal phase transition, which is accompanied by some Peierls-like distortion, charge ordering, anion ordering. The structural change is associated with a cell doubling, coupled with the important structural relaxation of the molecules with the degree of CT gives rise to a tetramerization process and bending of the neutral molecules: M phase : **… $D^{+0.5}D^{+0.5}$ $D^{+0.5}D^{+0.5}$… to I phase : …(D^0D^0 $D^{+1}D^{+1}$) …** Large optical reflectivity change induced by the irradiation of femtosecond (fs) pulsed laser (pulse width: 120 fs, photon energy: 1.55 eV, repetition rate: 1 kHz) were observed, using the optical pump-probe technique [3].

We investigated the structural signatures associated with the photoinduced transition from the I (low temperature) state to the M one, by the optical pump and x-ray probe technique, as we did for TTF-CA [1,2]. The crystal was illuminated by rather strong excitation light, and we were looking for changes in the intensity of the Bragg reflection as a function of the delay between the laser pump and the x-ray probe. Complete diffraction data were collected and the structures were solved and refined with good quality, and where in very good agreement with the already known structures at thermal equilibrium.





In order to excite a larger part of the crystal, we strongly increased the laser excitation density to the limit of the crystal damage. We worked on the smaller crystals we have (20 μm thick). We pushed the experimental set-up to the limit of what can be done, by developing a new laser excitation geometry with a double laser pulse excitation from the crystals at the bottom and top of the crystal (figure) in order to excite a larger fraction of the crystal, because of the limited penetration depth (estimated to few μm at this time). The two laser pulses were synchronized on the crystal on a time scale much smaller than the x-ray pulses (100 ps).

We made a large number of measurements on different crystals, but unfortunately, we could not observe any time dependence neither on the diffraction pattern, or on the structures measured before and after the laser excitation at different delays. It was only recently that the penetration depth of the laser was measured in an accurate way. It comes out that it is of the order of 0.1 μm. Therefore, we could not observe any change because the fraction of the crystal, which may be transformed, is of the order of few percent. The signal/noise ratio that we get on such small crystal, with quite long exposure time did not make it possible to observe such a signal.

We are now developing optical experiments to check if excitation at different wavelength can increase the penetration depth. However, the development made around the double pulse laser excitation will be very useful for future investigations, especially in other systems, since it makes it possible to double the fraction volume. Therefore the change of the diffraction signal, associated with the photoinduced transition, will be easier to detect.

References

[1] E.Collet et al., Science **300,** 612 (2003).
[2] L. Guérin et al., Chemical physics, **299**, 163 (2004).
[3] M. Chollet et al, Science **307** (2005).