ESRF	**Experiment title:** Time-dependent investigation of ultrafast structural modifications following photo-excitation of Tetrathiafulvalene-Tetracyanoquinodimethan .	**Experiment number**: CH 2276
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Report:

In the proposal for this beam time we aimed at investigating structural changes of TTF-TCNQ crystals after photo-excitation. The experiments were planned to be carried out in pump-probe mode with the optical laser pump to excite the sample and thus initiating structural changes. The Helijet (oxford diffraction) could not provide stable temperatures near the phase transitions between 30 K and 60 K and the Helijet induced a rapid ice growing at the sample. So we skipped the experiment and measured time resoved structural changes in TTF-CA crystals after photo excitation. The neutral to ionic phase transition occurs at 81 K. With the nitrogen cryojet (oxford diffraction) the temperature of the sample could be stabilized at 100 K. The intensity of the laser-pulse was I_{Laser} = 35 ± 15 mW/mm^2 and the focal diameter was d = 1.25 mm. The temperature increase for a mean intensity of 40 uJ per pulse at 80 K is between 14 K and 1.4 K per laser pulse for a penetration depth between 1 um and 10 um. The current of photons at the sample for an intensity of the laser pulses of I_{Laser} = 35 ± 15 mW/mm^2 is $I_{photon} = 1.1 \pm 0.5 \cdot 10^{16}$ photons/cm^2. This value needs to be compared to an intensity $I_{photon} \approx 1.7 \cdot 10^{16}$ photons/cm^2, above which photo-induced phase transition can be observed according to Collet et al. [1]. In [1] it is further stated that below $0.7 \cdot 10^{16}$ photons/cm^2 no photo-induced phase transition effect is to be observed. The repetition rate of the laser was n = 1000 Hz and the polarization at the sample position was in the plane of the optical table. The wavelength of the laser was around 660 nm with a width of ~ 10 nm. The bandwidth of optical femtosecond lasers is nearly 10 nm. The wavelength of the x-rays were λ= 0.688801 Å, this means a photon energy of 18 keV. The number of photons per pulse was N= 10^6 and the repetition rate of the x-ray pulses were 1000 Hz. The experiments were carried out in the 8×24 + 1 bunch mode. The relative bandwidth is ~ $3 \cdot 10^{-4}$. The TTF-CA samples were grown in an oversaturated solution of extreme pure acetone, Uvasol. The grown crystals had a size of 3 mm × 200 um × 100 um. For measurements they were cut to a size of about 200 um × 100um × 20um. We also investigated much smaller crystallites improving thus the signal-to-noise ratio.

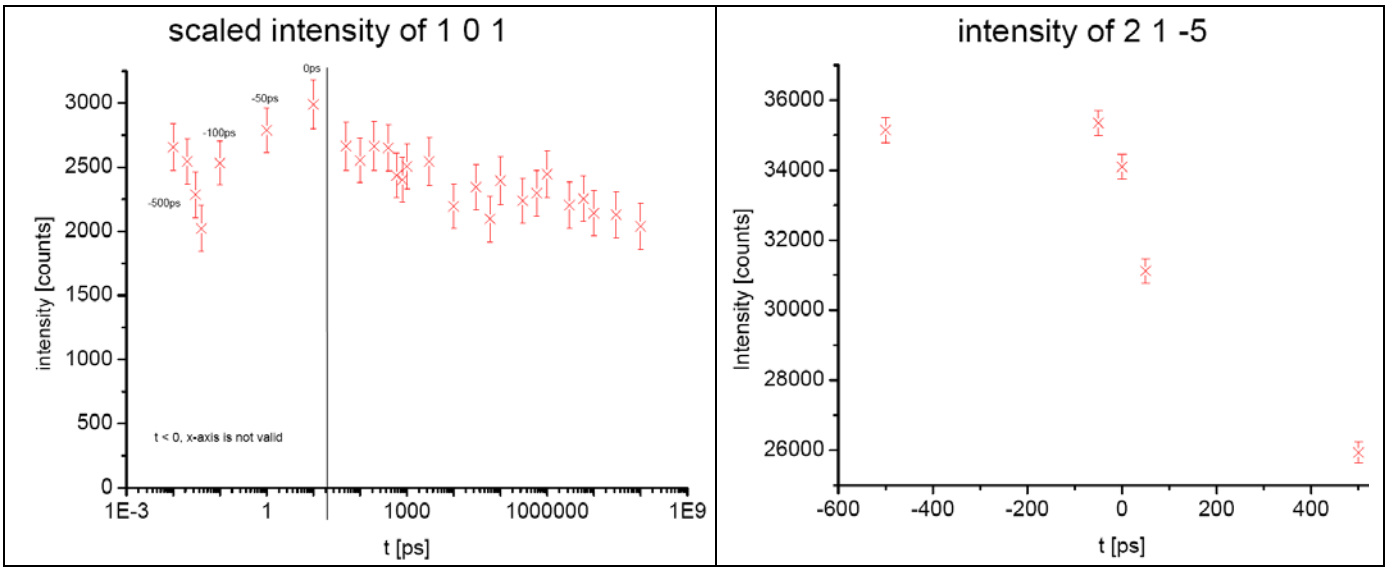

Fig.1: Left: Integrated intensity of 1 0 1 reflection against time delay . The time delays on the left side of the figure are not related to the time-axis and values are written directly above the data points. The first four data points on the left side of the figure were all taken at a time delay of -500 ps. Right: Integrated intensity of the 2 1 -5 reflection of a much smaller crystallites against time delay.

We compared the static structure factors for TTF-CA for both phases at 40 K and 90 K [2] and identified the 1 0 1 reflection as a good candidate for pump probe measurements. Figure 1, left shows the time dependent development of the integrated intensity of the 1 0 1 reflection for the large crystal. The integrated intensity was determined using the FIT2D program. The intensity was corrected with respect to beam current in the ESRF storage ring. The intensity has a tendency of decay with real time of the measurement. The four data points at -500 ps were performed equally distributed between the beginning and the end of the measurement sequence. At this time delay no photo-induced effect is expected but the data show a clear decay. This decay might be due to crystal damage by laser irradiation. With exception of the data points from -50 ps to +50 ps we cannot identify a photo-induced signal in the data. The peak between -50 ps and +50 ps is not significant.

We also investigated five little TTF-CA crystallites with the same parameters (see also [3]). The volume of the crystallites was ~ 35 times smaller than the volume of the large TTF-CA crystal. In this experiment a time-resolved effect has been observed. Figure 2 shows the decay of the integrated intensity of the 2 1 –5 reflection against time delay. A problem of the measurement is that the angular range not necessarily contains 99% of the integrated intensity. Several reflections have been observed like this and both, decay and increase, could be observed as function of time delay, similar to the measurement by Collet et al. [1] and Guerin et al. [4]. In reference to the article of Collet et al. our observation might make sense: With a laser photon intensity between $I_{photons} \approx 0.6 \cdot 10^{16}$ photons/cm^2 and $I_{photons} \approx 1.6 \cdot 10^{16}$ photons/cm^2 we are in the regime where the photo-induced effect is only about to start. The collective effect still is very weak: The first rows of domino stones try to topple the next rows but succeded only in making them toddle. An explanation, why a photo-induced effect was observed from the TTF-CA crystallites might be that the thickness of the crystallites is small enough to observe a photo-induced signal from the sample volume corresponding to the laser penetration depth. This way we might not need to have a collective effect exciting the entire crystal via the domino effect.

References

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