ESRF	**Experiment title:** Time-dependent investigation of ultrafast structural modifications following photo-excitation of Tetrathiafulvalene-Tetracyanoquinodimethan .	**Experiment number**: CH 2276
Beamline: ID09B	**Date of experiment**: from: 14 September 2006 to: 17 September 2006	**Date of report**: 27. Feb 2007
Shifts: 9	**Local contact(s)**: Friederike EWALD	*Received at ESRF:*

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Report:

The proposed experiment aimed at investigating structural modifications of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) near one of the low temperature phase transitions (30-60 K). The experiments were planned to be carried out in pump-probe mode with the optical laser pump to excite the samples and thus initiating the structural changes. Unfortunately it turned out that the required cryogenic Helium jet device (Helijet), required for cooling, maintaining and controlling the temperature was not available for the experiments. Since no other cooling method for this temperature regime was at hand, the plan for the experiment had to be revised largely. Since this change of plan became clear only the week before the experiment it was not possible to design a completely different experiment. Also it was too late to give the beamtime slot to another group. Instead we decided, in agreement with the beamline responsible M. Wulff, to use the beamtime slot for three smaller experiments plus some time for preparation of future studies.
All experiments were carried out in the 8×24 + 1 bunch mode. This seemed to work nicely and problems occurred neither with the fast shutter nor stability of the x-ray beam.

1. Measurements at TTF-TCNQ at elevated temperature between 80 and 295 K:
For these measurements we could use the liquid N_2 jet available at ID09. First we checked that the indexation of the samples at the instrument was possible and straightforward. A fast indexation at the instrument is required to find specific reflections which shall be investigated *on-peak*. This method of observing the change of reflectivity of specific reflections is important for experiments exploiting much shorter pulse durations and smaller repetition rate. Here the rotating crystal method, varying the orientation of the sample with respect to the x-ray beam, will not work and other methods have to be applied. One possibility is the observation of changes of the peak reflectivity without the need to rotate the crystal. In Fig. 1 an indexed pattern for T = 150 K is given and Tab. 1 indicates the refined cell parameters in comparison to literature values. In summary the indexation works sufficiently well and can be used in further experiments to orientate samples at ID09 without causing significant loss of beamtime.
We have selected a temperature of 150 K since at this temperature diffuse scattering originated by $2k_f$ diffuse sheets should become observable [1]. A preliminary time-resolved optical laser pump x-ray probe experiment did not produce observable intensity changes for the Bragg reflections. But these were only initial measure-

ments not optimized and shall be repeated under optimized conditions. Excitation of the samples was achieved using the optical laser at 532 nm wavelength with an energy of 30 μJ in a spot of ~1 mm^2.

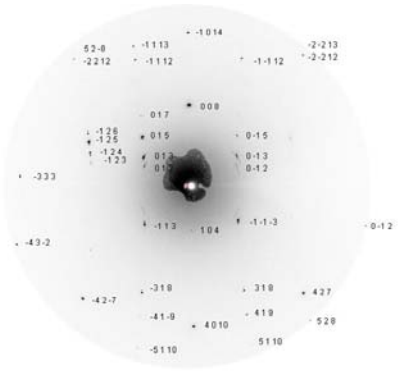

Fig. 1: Diffraction pattern of TTF-TCNQ at 150 K including indexed reflections.

	295 K	150 K	100 K	60 K	53 K	40 K
a	12,302(6)	12,242(7)	12,228 (6)	12,173(10)	12,191(10)	12,210(5)
b	3,817 (1)	3,772(5)	3,754 (1)	3,733 (2)	3,731 (2)	3,729 (1)
c	18,449(9)	18,379(33)	18,379(10)	18,301(10)	18,312(10)	18,343(6)
γ	104,49 5)	104,49(15)	104,42(4)	104,33 (2)	104,43 (2)	104,38(2)
V(Å^3)	838,7 (3)	821(32)	817,0(7)	805,8 (8)	806,6 (8)	809,0 (5)
ρ (g/cm^3)	1,62	1,65	1,66	1,68	1,68	1,68

Tab. 1: Comparison of cell parameters. Values for 150 K are from this measurement, for 295 K from [2], for 100 K and 40 K from [3] and for 60 K and 55 K from [4].

Finally we aimed to measure time-resolved diffraction at 80 K, the lowest temperature we could acieve using the available N_2 cryostream. These experiments used similar laser parameters and were started during the last shift. It turned out that alignment was not correct and that the crystal was not properly centered on the rotation axis. Unfortunately the crystal went out of the beam during oscillation and the imcomplete data set could not be analysed.

This experiment suffered strongly from the fact that the cryojet was not available. It has to be repeated as soon as possible. We will request beamtime for the diffuse scattering investigations in Mar 2007.

2. Measurements of powder diffraction from MAMC

Powder diffraction from methylammonium tetrachloromanganate (MAMC) was carried out as part of our campaign to study photo-induced phase transitions in these compounds. In a previous attempt (MI-788) we could observe scattering patterns only for the room temperature phase. The cryogenic N_2 jet was used to set the sample temperature near the structural phase transition a 257 K. A new, airfree sample container was tested. Due to the short announcement, we could not provide a finally tested environment, but only a preliminary version. In this device the N_2-jet cools the layered sample from one side while a N_2-gas nozzle provides a water free environment from the other side. It turned out that still a thin layer of ice formed, probably because the N_2 flow was not yet optimed and air penetrates into the container. The ice gave rise to characteristic diffraction pattern and at longer times the sample dissolved by water. We will continue with the design of the sample container and ask for more beamtime in 2007. The results obtained in a preliminary time-resolved pump-probe experiment are summarized in the experimental report for MI-788.

3. Measurements of 2-(α-Styryl)pyrylium salt (StyPy) single crystals

In accordance with the beamline responsible part of the beamtime has been swopped with experiment CH-2407 and will now be performed in May 2007. During the reported beamtime, essentially the results reported in CH-2174 could be reproduced when furthermore systematic studies on the excitation conditions have been performed. Further details will be given in the report for CH-2407 upon completion of the experiment in Spring 2007.

References

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