ESRF	**Experiment title:** **Enhancing functionality of combined fast calorimetry / nano-focus X-ray scattering setups**	**Experiment number**: SC-3898
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Shifts: **2014/II 9**	**Local contact(s)**: Martin Rosenthal	

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This report concerns the progress of the project from the first four months of LTP-SC-3898

Introduction:

The present project is devoted to further development of the combined X-ray scattering/fast calorimetry setup allowing to simultaneously address the thermos-physical and structural parameters of nanogram-sized samples. It is noteworthy that the proposal has been submitted in continuation of our previous LTP, SC-3457, in which the first prototypes of the nanocalorimetric accessories have been designed, built and commissioned to the ID-13 beamline. The in-situ use of the nanocalorimetric accessories in combination with the nano-beam X-ray scattering has been proven useful for the user community (cf. the final report on LTP SC-3457) and was judged to deserve further enhancement in order to make it compatible with fast X-ray detection and also with an in-situ cryo cell allowing to perform nanocalorimetric measurements at low temperatures.

Generally, the MEMS-based chip calorimeters were shown to be a powerful technique for probing extremely small quantities of materials, since the original development by Prof. L. Allen. The technique has been already successfully applied to studies of metals, thin and ultra-thin films of amorphous and semicrystalline polymers, self-assembled monolayers, individual biological objects and explosives in the state of traces. It is noteworthy that the sensitivity of the calorimetric sensor can be pushed to the nano-gram and even pico-gram range due to the use of extremely fast cooling/heating rates (up to 108 K/s) that are completely inaccessible by the conventional calorimeters such as Differential Scanning Calorimeter (DSC). If judged from the point of view of bibliometry, the nanocalorimetry applications are rapidly extending, if one judges it from the point of view of bibiliometry, the field of nanocalorimetry is now at the stage of the exponential expansion. Nevertheless, it is a recent method in the stage of development, which has not yet become routine, and the community expects from it in the next years to become more quantitative and robust.

It is important to mention that, over the last one-two years, there is more and more interest of the scientific community in the use of combined Nanocalorimetry and X-ray scattering setups. However, till now, there was only one commercial Nanocalorimeter instrument (Flash DSC from Mettler-Toledo) available on the market. This device has not been developed for such instrumental combination. Moreover, the design of this calorimeter fully excludes the possibility of any in-situ X-ray measurements.

Milestones for first Year:

In the first 4 month, and in agreement with the milestones for the first year of the project, low-temperature nanocalorimeter cell compatible with the nanocalorimeter setup developed in the frame of the LTP SC-3457 meeting the requirements of the ID13 Micro-Hutch experimental stage was developed. In a second step, first experiments using the fast acquisition modes of of the MAXIPIX and the FreLon detectors present at the beamline were tested using a standard test sample of polytrimethylene terephthalate. During this experimentation, different measuring protocols were tested. A final evaluation of the protocols and the low temperature stage performance as well as the expansion to other materials is planned for the first halve of the experimental round in 2015.

1. Design of the low temperature cell for Nano-calorimetric sensors

During the first months of the LTP we have finalized the design of the low-temperature nanocalorimeter cell adapted to the ID13 experimental end stations. The fabrication of the single components of the low temperature cell is finished. A revised design of the low temperature cell is shown in Figure 1.

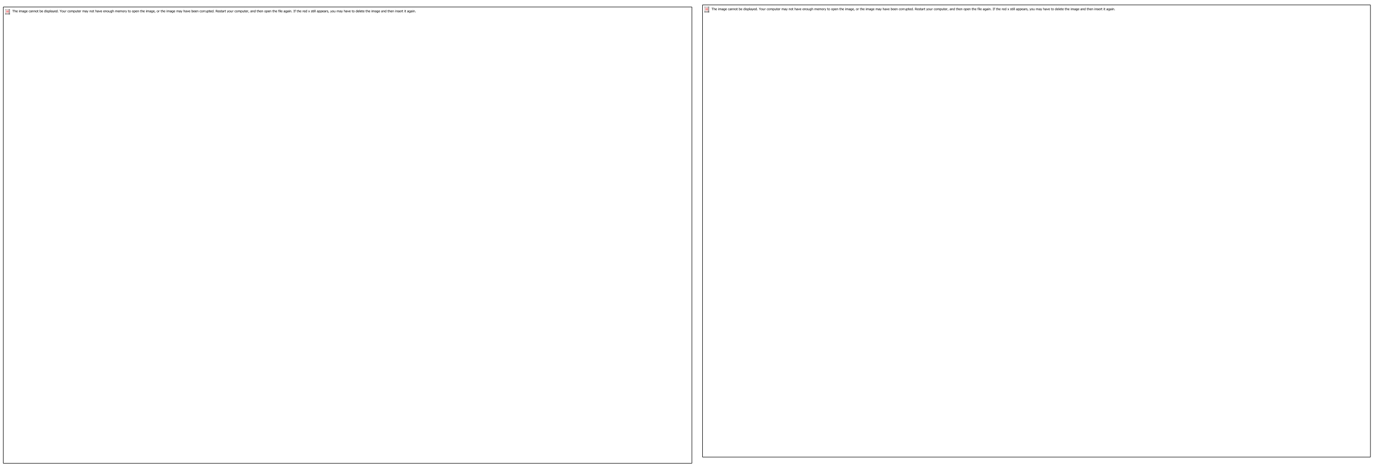

Figure 1. 3D model of the revised low temperature cell compatible with the standard nanocalorimeter chips in assembled and disassembled state.

The housing of the low temperature cell consists of solid aluminium plates to assure a fast and homogenous temperature equilibration of the cell with the experimental station of the ID13 micro hutch. The inner part of the chamber consists of INVAR shell entwining a copper core. The choice of INVAR is explained by the low thermal expansion of the material while having a relatively low thermal conductivity with respect to other metals. The copper core of the stage allows a fast equilibration of the temperature around the nanocalorimeter chip. The cooling of the copper block will be achieved by flushing cold nitrogen from a not pressurized liquid nitrogen dewar using cold gas pumps downstream the low temperature stage. The exact temperature adjustment in the copper core will be acquired using PID controlled electrical heating cartridges. The fabricated and disassembled parts for the cell are shown in figure 2 left.

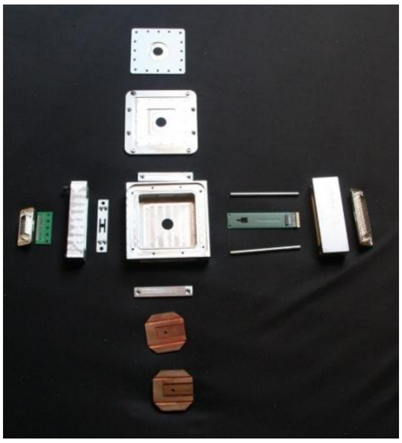

Figure 2. Fabricated and disassembled parts for the low temperature cell (left) and assembled prototype (right).

A test implementation of a preliminary assembly of the low temperature cell was done during the first beamtime of the LTP in the end of December 2014. The final implementation of a revised version of the low temperature cell is scheduled for year 2. The associated re-design the optical apertures and collimators of the micro hutch of the ID13 beamline to meet the special requirements of the low temperature stage is in process and will be finalized in collaboration with the beamline staff in the first halve of 2015.

2. Approaching fast acquisition of scattered signals emerging from nano-gramm sized nano-calorimetric samples

In parallel to the design and fabrication of the low temperature cell a preliminary experimental test was performed using a fast-pixel-area detector (MaxiPix) present at the beamline in order to meet the time scales of the ultra-fast calorimetry. At the first stage of the experiment a beam with the crossection of 20x20 μm^2 was used to match the size of the measured sample. The rather big beam was chosen in order to minimize the local damage of the sample caused by an intense focused beam while keeping the amount of scattered X-ray photons as high as possible. This approach does not target measurements where a high special resolution of structural information is needed, but to experiments targeting the acquiring of integral information of fast structural changes in the sample. The data analysis of the acquired data is in process right now and will be finished in the next weeks. The results will help to optimize the experimental conditions for the next stage of the project where we will apply a combination of fast DC nanocalorimetry and micro- and/or nano-focus X-ray diffraction to explore the thermal stability of sharp oligomers of 3HT and the corresponding P3HT, which is the archetype of a polymer semiconductor being used for field-effect transistors and solar cells. In particular, we will study dip-coated and spin-cast films of P3HT and its corresponding $(3HT)_n$ oligomers.

In addition, the capability of the nanocalorimetric setup to work at low temperatures was tested using the cryo-stream setup present at the beamline. Therefore, the nanocalorimetric sensor was placed in the working point of the cryo-stream and a constant flux of low temperature nitrogen was purged on the sensor, while the temperature response of the sensor was recorded in modulation. The temperature amplitude and phase signals of the sensor response, as well as the temperature offset to the surrounding of the on chip thermopiles and heaters are given in figure 3 with and without cryogen nitrogen flux, top and bottom respectively.

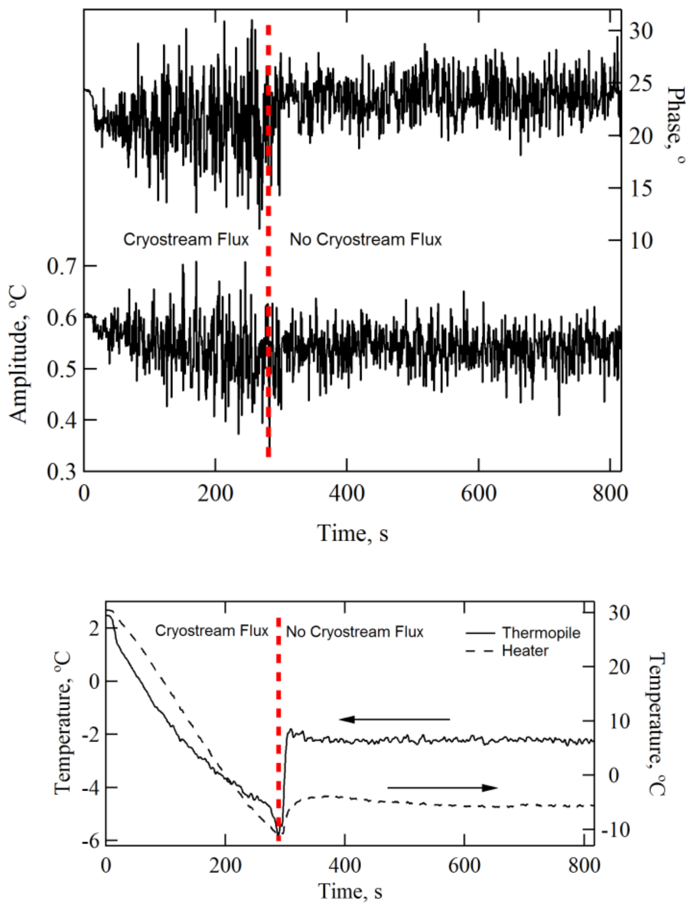

Figure 3. Temperature amplitude and phase signals of the on chip thermopiles and heaters (top) and temperature offset to the surrounding (bottom) measured in modulation mode for a sensor being exposed to a cryogen nitrogen flux (left) and with no flux (right).

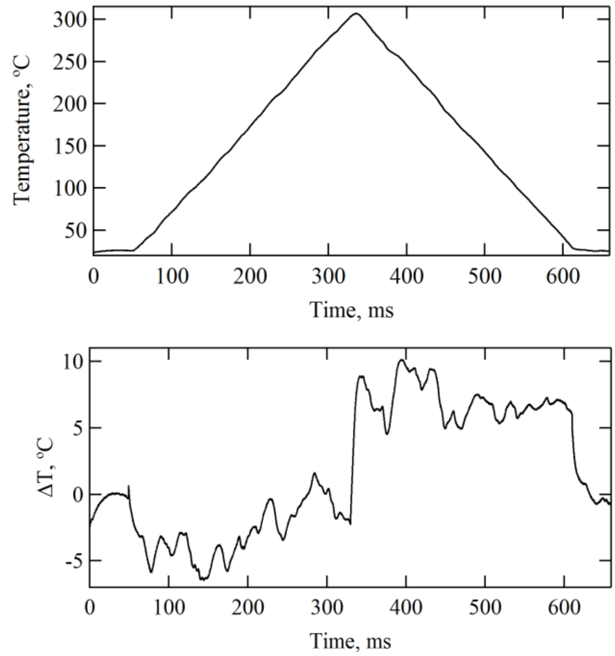

Figure 4. Temperature profile of a fast heating-cooling experiment under purge of a cryogenic nitrogen flux on the sensor.

The measurements show, that the nanocalorimetric sensor is opperational in AC-mode (modulated calorimetry) at low temperatures using the cryo-stream setup on the expenses of a slightly increased noise level on the temperature amplitude and phase signals. However, when operated in ultra-fast calorimetric mode some temperature stability issues appear due to the non-perfect constancy of the purged nitrogen flux increasing the error on the temperature signal drastically as shown in figure 4. The temperature curve of the empty sensor purged with the cryogen nitrogen flux, given in the top of the graph, shows visible temperature instabilities during the fast heating and cooling. When subtracting the same temperature profile recorded without nitrogen flux the temperature instabilities can be identified to be 5.15°C in standard deviation.

2. Conclusions

In agreement with the 1^{st} milestone defined for the first year of the LTP a low-temperature nanocalorimeter cell compatible with the nanocalorimeter setup developed in the frame of the LTP SC-3457 was developed and fabricated at the Moscow State University. The prototype was undergoing during the first experiment conduced in the micro hutch facility of the ID13 beamline during the time from the 14/12/2014 to 16/12/2014. In agreement with the 2nd milestone first experiments were conducted on nano gramm sized samples using fast detection modes and a 20x20 μm^2 beam.

The development of an optimized setup for *in-situ* fast nanocalorimetry nano/microfocus X-ray diffraction experiments using millisecond time resolution is planned in preparation for the next beam time scheduled in spring 2015. Design of measuring protocols for *in-situ* fast nanocalorimetry nano/microfocus X-ray diffraction experiments including data acquisition issues, synchronization and data handling will be continued in order to provide the possibility to study nucleation mechanisms in energetic materials as defined in the 4^{th} milestone of year 1, while the first first fast DC calorimetric/micro-focus X-ray diffraction *in-situ* experiments on thermal stability of P3HT and corresponding (3HT)n oligomers are planned for the end of the year 2015.

From the test experiments using the cryo-stream setup installed at the ID13 beamline in the micro-hutch it can be seen that slow and moderate heating experiments using a cryogenic nitrogen flux on the heating sensor are possible. However, the quality of the thermal signal is suffering from the perturbations brought into the setup by the non-perfect constancy of the nitrogen flux. On the other hand, the perturbations due to the nitrogen flux make fast calorimetric experiments difficult showing that a cryo-cell without perturbing gas flow is needed to conduct useful in-situ Nanocalorimetry-Nanobeam experiments.