ESRF	**Experiment title:** Time resolved powder diffraction of photoactivated MAMC in spinning and non-spinning sample environments	**Experiment number**: MI-788
Beamline: ID09B	**Date of experiment**: from: 12 July 06 to: 14 July 06	**Date of report**: 28/02/07
Shifts: 9	**Local contact(s)**: Michael Wulff	*Received at ESRF:*

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Report:

Powder diffraction studies on MAMC (methylammonium tetrachloromanganate (II) $[(CH_3)(NH)_3]_2MnCl_4$) were proposed to investigate the possibility of retrieving time-resolved structural data following photo-excitation in the presence of preferred orientation effects. To investigate the effect of preferred orientations we proposed to compare results for a spinning sample, standard procedure to average out preferred orientation effects, with those of a non-spinning sample. Ideally, in the difference data sets of the pump-probe experiment the preferred orientation effect would cancel out and both data set would give similar results. MAMC was selected for these measurements due to its scattering power and the richness of the structural phase diagram [1,2]. Critical for these experiments is the temperature of the powder that must be near a phase transition temperature thus reducing the required activation energy and making the photo-induced process more efficient. We chose the RT → LT transition at 257 K which can be easily reached using a N_2-open flow cryo system. Out of the 12 shifts accorded by the review committee only 9 could be allocated for beamtime due the problem with asbestos and the consequent loss of available beamtime.

The experiments were carried out in optical pump–x ray probe mode and detecting the powder diffraction using the MAR CCD detector geometry was conducted at ID09. The optical laser wavelength was set to 532 nm with an energy of 16 μJ. The focal spot size of the nearly co-propagating laser beam on the sample was ~ 2 mm. The wavelength of 532 nm corresponds to off-resonant excitation thus increasing the penetration into the sample. Samples were prepared as an approximately few μm thin powder film on polyamide film. This substrate gave only very small contribution to the scattering pattern. In a previous pump-probe experiment this method worked well, but in the reported experiment we used an open cryostream and observed the problem of ice formation and degradation of the hygroscopic samples. Only data for room temperature could be taken, which are not expected to show the photo-induced effect. After this beam time we started the design of a sample container to keep the samples dry and ice free during refrigeration. The container includes one nozzle to blow dry nitrogen on the backside of the sample and also introduces the cold nitrogen stream cooling the sample side. We had planned to ask for additional beamtime in 2007, but due to rescheduling we could use part of the beamtime during CH-2276 (see report for CH-2276). Unfortunately our new system was neither ready nor tested by then and it turned out that still too much air penetrates into the container leading to ice formation and sample degradation. The container design therefore has to be improved.

For the experiment we therefore decided to focus on time-resolved measurements without rotating the sample. In this configuration the air flow can be better stabilized and ice formation is strongly surpressed. We aimed to determine a distinct fingerprint of the phase transition close to 257 K and to follow the change of peak shape and intensity time-resolved following photo-excitation. Fig. 1 (left side) shows the integrated diffraction pattern measured at a photon energy of 18 keV (0.689 A) in the angular regime near the 200 and 020 reflections. In the room temperture phase both reflections are clearly seperated while in the cold temperature phase both reflections occur at the same angle. Two additional reflections in the cold phase could be identified as ice rings. Simulated diffraction patterns (Fig.1, right) do not account for preferred orientation and show smilar behavior as found for the 200/020 reflections. From the simulation the 114 reflection should be visible with a high l value of 4. We take this as an indication of the preferred orientation of the sample.

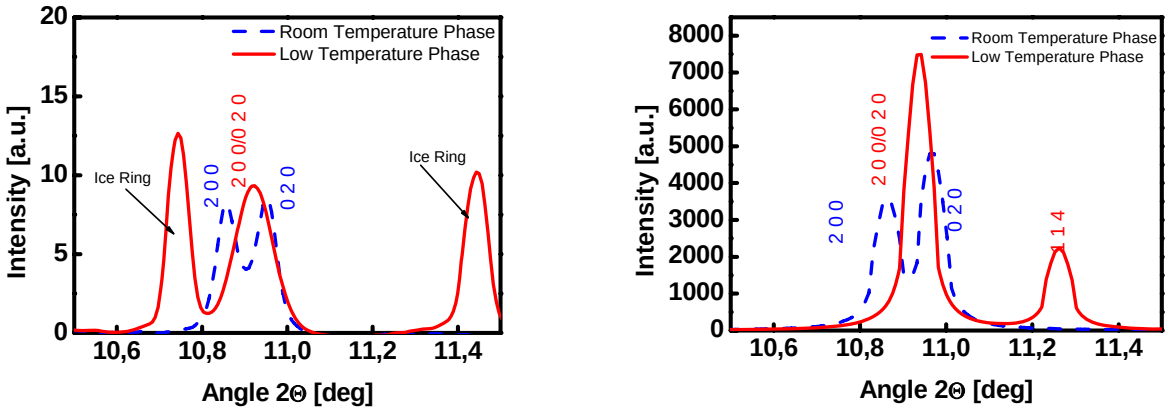

Fig 1: Experimental powder diffraction pattern after integration and substraction of background (left) and simulated pattern for room and low temperature phases.

At this temperature below the phase transition time-resolved measurements for delays between -200 and 800 ps were performed. The time-dependent integrated intensity of the 200/020 reflection, determined by fitting the diffraction profile with a gaussian function, is shown in Fig. 2. Within the statistical accuracy of our data we do not observe a time dependence. This preliminary result will be complemented by further analysis of other reflections also showing the static phase transition. We also will verify if the excitation conditions and possible sample degradation may have affected the result of the measurement. Finally, it will be important to repeat the measurement with the possibility to compare data from spinning and non-spinning samples.

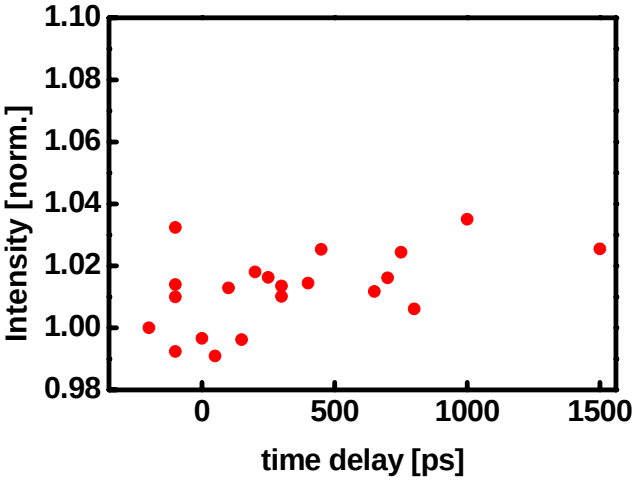

Fig 2: Integrated intensity of the 200/020 reflection as a function of delay time between laser and X-ray pulses.

References

[1] C. Blome, Th. Tschentscher, J. Davaasambuu, P. Durand, S. Techert, J. Synchro. Rad. **12**, 812 (2005)

[2] C. Blome, Th. Tschentscher, J. Davaasambuu, P. Durand, S. Techert, AIP Conf. Proc. **879**, 1254 (2007)