



	Experiment title: Investigations on the Dynamics of the Jahn Teller Distortion in TMA-Manganese Compounds	Experiment number: CH 1745
Beamline: ID09B	Date of experiment: from: 26 November 2004 to: 29 November 2004	Date of report: 15/08/2006
Shifts: 9	Local contact(s): Dr. K.-Y. Kong	<i>Received at ESRF:</i>
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Report:

In **CH1745** we studied the structural response function of $(\text{MA})_2\text{MnCl}_4$ and $(\text{TMA})_2\text{MnCl}_4$ with $\text{MA}=(\text{CH}_3)_3\text{H}_3\text{N}^+$ and $\text{TMA}=(\text{CH}_3)_4\text{N}^+$ upon photoexcitation. As method, time-resolved powder diffraction was employed.

In both systems transient signal changes were discovered which were both on a quite fast time scale. Furthermore, in $\text{MA}=(\text{CH}_3)_3\text{H}_3\text{N}^+$ we investigated its long-time behaviour on the millisecond time scale. Figure 1, left summarises a typical powder diffraction pattern after integration with Fit2D. The structure analysis of the time-dependent XRD data revealed a stretching of the MnCl_6 octahedra in $(\text{MA})_2\text{MnCl}_4$ powder after photoexcitation in the magnon sensitive band at 420 nm. The refinement resulted in a axial Mn-Cl bond length stretch from 2.51 Å in the ground state to 2.78 Å in the excited state, which are quite pronounced but also typical changes for MnCl_6 after optical photon absorption (if polarons are involved). The occupancy of the photo-excited state was refined to be 15 - 20 % [1,3].

We explain the de-population of this state at 300 ps with energy redistribution processes and thermal energy dissipation into the whole crystallites of the powder.

For longer time-scales, on the micro- to millisecond time scales, also population of Mn-Cl stretched states were found with 5 - 8 % occupancy. We assign them to the creation of for Mn typical triplet states whose electronic lifetime are known to be about 200-500 us (from our optical spectroscopic investigations).

$(\text{TMA})_2\text{MnCl}_4$ do show even more pronounced transient signal changes. However, in this system the time-dependency is quite different from $(\text{MA})_2\text{MnCl}_4$: within the first 200 ps, an intermediate is created which lives quite long and decays with a time constant of some hundred nanoseconds. The structural refinement yields in a major distortion of the tetrahedra towards each other rather than within a tetrahedra which is in contrast to the photo-excitation behaviour of $(\text{MA})_2\text{MnCl}_4$ and explains the major signal changes [4].

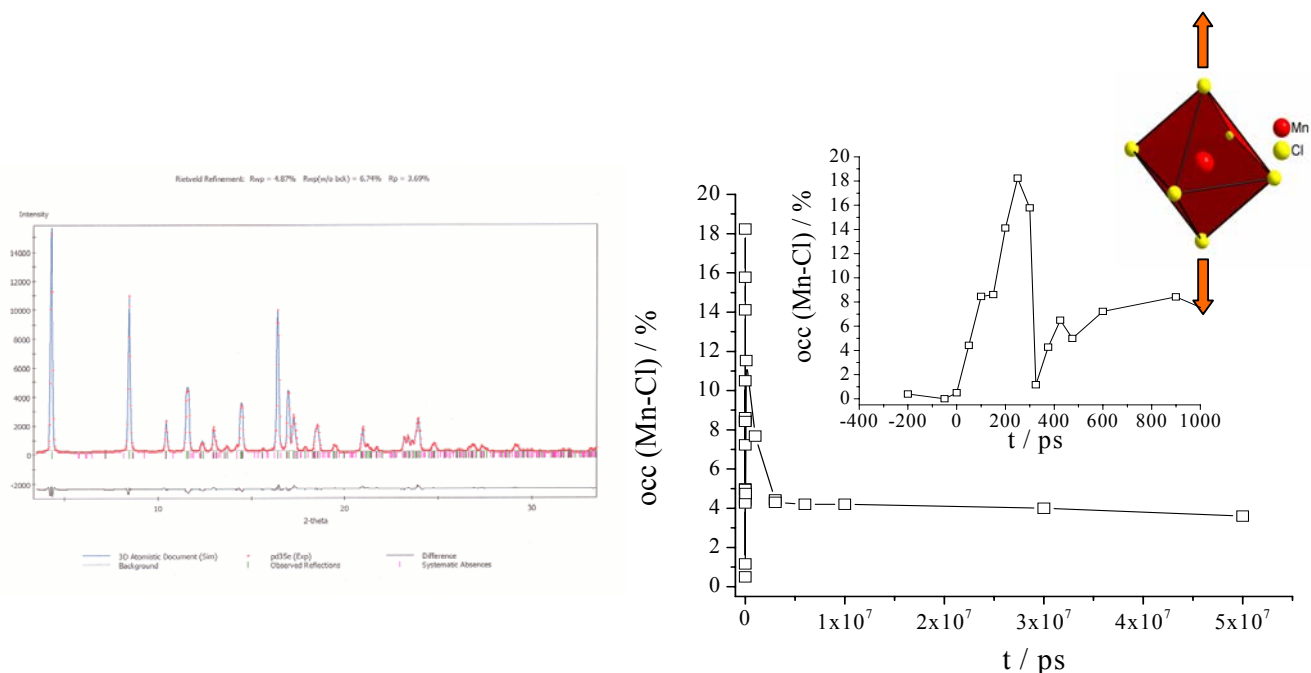


Figure 1: Left: Typical powder diffraction pattern of $(MA)_2MnCl_4$ upon photo-excitation and after integration of the 2D diffraction pattern. Right: Result of the data evaluation: rising and decaying times of intermediate states which are characterised by Mn-Cl stretches of the axial Cl atoms in the $MnCl_6$ octahedra.

One can summarise that it is possible to follow photo-induced structural changes of 2D perovskite-type of layered crystals with powder diffraction if one is working beyond the laser threshold which might introduce photo-selective burning effects [3]. The results of this beamtime will be published elsewhere [3,4] and is of fundamental interest for the development of time-resolved powder diffraction strategies on the ultrafast time scale [5,6].

References

- [1] P. Durand, S. Techert, *Acta Cryst. A*, **60**, S77 (2004).
- [2] P. Durand, Th. Tschentscher, S. Techert, *J. Appl. Cryst.*, *submitted* (2006).
- [3] P. Durand, Q. Kong, S. Techert, *to be submitted* (2006).
- [4] P. Durand, Q. Kong, S. Techert, *in preparation* (2006).
- [5] C. Blome, Th. Tschentscher, J. Davaasambuu, P. Durand and S. Techert, *J. Synchrotron Rad.* **12**, 812–819 (2005).
- [6] C. Blome, Th. Tschentscher, J. Davaasambuu, P. Durand, S. Techert, *Syn. Rad. Instr.*, *in press* (2006).