Experimental report

16/09/2019

Proposal: 5-54-284 **Council:** 10/2018

Title: Reversible magnetoelectric switching by electrochemical lithium intercalation

Research area: Physics

This proposal is a new proposal

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Samples: La0.5Sr0.5MnO3
La0.5Sr0.5MnO3/La0.66Li0.33TiO3/LiNbO3/Au
Li0.1La0.5Sr0.4MnO3

Instrument	Requested days	Allocated days	From	To
D17 He3 Spin Filter	4	2	31/08/2019	02/09/2019

Abstract:

The aim of the project is in the long run to observe the relation between charge ordering and magnetism in manganites. La1-xSrxMO3 shows transitions between ferromagnetism (FM) and paramagnetism at room temperature and between antiferromagnetism (AFM) and FM at lower T for x roughly 0.5. It is believed that the driving force is the ordering of Mn3+ and Mn4+, which sets in at x about 0.5. Our approach is to reversibly change the Mn3+ / Mn4+ ratio by de-/lithiating the material electrochemically and to monitor the process in-situ with Polarized Neutron Reflectometry (PNR).
Samples of various compositions were grown by Pulsed Laser Deposition and characterized structurally and electrochemically. The first in-situ PNR measurements at Amor (PSI) with a liquid electrolyte gave hints that LSMO undergoes the phase transition.
We want to perform further PNR measurements using a solid state electrolyte to prove the reversibility of the process by performing several de-/lithiation cycles and by monitoring it in-situ. A repetition at low temperatures (150 K) then probes the interesting transition FM/AFM.

Reversible magnetoelectric switching by electrochemical lithium intercalation

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The aim of the project is to observe the relation between charge ordering and magnetism in manganites ($A^{3+}_{1-x}B^{2+}_{x}\mathrm{MnO_3}$). They show complex phase diagrams as a function of composition x and temperature T with a variety of magnetic and electronic phases. $\mathrm{La_{1-x}Sr_xMnO_3}$ (LSMO) shows transitions between ferromagnetism (FM) and paramagnetism at room T and between antiferromagnetism and ferromagnetism at lower T at $x \approx 0.5$ and an even ratio of $Mn^{3+/4+}$. As it is believed that the latter is the leading parameter for those phase transitions. Our approach is to reversibly change this ratio by de-/lithiating the material electrochemically, using a Li-ion battery-like all-solid-state thin film cell and to monitor the process in-operando. Alternatively, we used the already lithiated material $\mathrm{La_xSr_yLi_zMnO_3}$ (LSLMO) starting on the FM-side of the phase boundary. 30 nm thin films of compositions $\mathrm{La_{0.5}Sr_{0.5}MnO_3}$ and $\mathrm{La_{0.5}Sr_{0.4}Li_{0.1}MnO_3}$ were grown on 10x5x1 mm^3 conducting $\mathrm{SrTiO_3:Nb(0.5\%)}$ by Pulsed Laser Deposition, and were proven to be epitaxial by X-Ray Diffraction. To determine the magnetic states of the virgin samples Polarized Neutron Reflectometry (PNR) measurements were carried out at room T on the instrument (D17). The films were then electrochemically characterized. For the in-operando PNR measurements an electrochemical needle probe station was designed and built (see fig. 1). We were able to measure 4 samples in total with slightly different compositions (LSMO/LSLMO). During the measurements, voltage pulses were applied. Reflectivity was recorded for two hours while the spin states were switched every ten minutes. After that the next current pulse was applied:

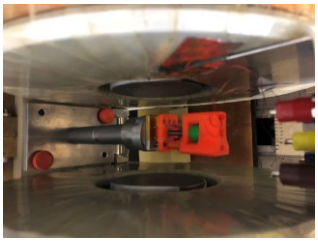

Figure 1: electrochemical cell

1) De-/lihtiation of LSMO: no changes in magnetization where observed. This could be due to the electronic nature of the sample (not conductive enough). A solution would be to introduce a conductive buffer layer between the substrate and the LSMO layer, like $\mathrm{LaNiO_3}$.
2) De-/lithiation of LSLMO: A change in magnetization was observed for sample GB96_Li (see fig. 2 & 3). Only 50% of the samples' area is contacted for electrochemistry because the multilayer is patterned in a way to avoid short circuiting. Thus, the actual magnetic signal is expected to be smaller because the whole sample is exposed to the neutron beam. A doubling of the spin asymmetry would therefore result in a tripling within the contacted area. However, reversibility could not be proven because the beam time ended.

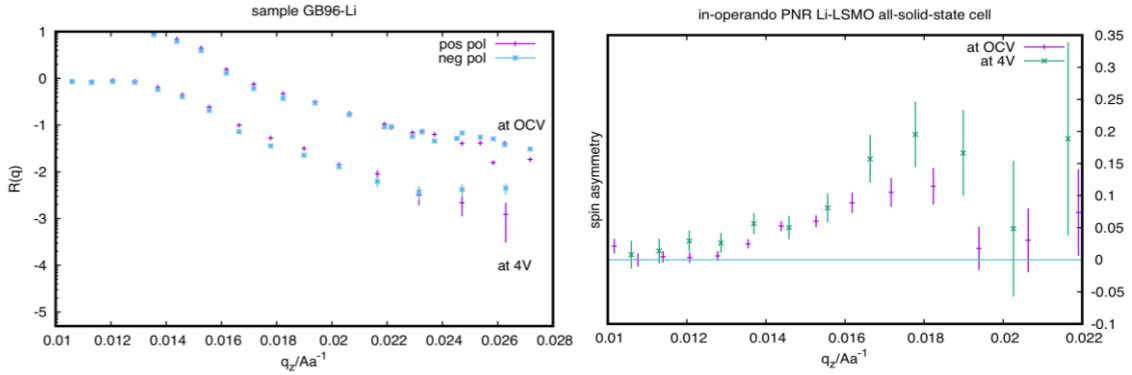

Figure 2 and 3: reflectivity and spin asymmetry for an LLSMO sample at OCV and 4 V

Resume: The in-operando PNR measurements using the needle probing station (see fig. 1) are working. We monitored the expected magnetic effect for the LSLMO (see fig. 2 & 3). But we yet could not prove the reversibility of the process. Additionally, cooling was not possible due to shortness of time. In the future, we want to use the solid cell stack again but use a conductive interlayer because the current transport might be kinetically favored when $\mathrm{LaNiO_3}$ is used as a current collector. Further measurements at low T (150K) to probe the FM/AFM transition should be performed in the future.

Work fully performed at ILL
Proposal number: 5-54-284
Instrument: D17