Experimental report

12/07/2023

Proposal: 5-54-385 **Council:** 10/2022

Title: Room temperature hydrogenation process and its effect on the magneticproperties of overdoped La1-xSrxMnO3.

Research area: Materials

This proposal is a new proposal

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Experimental team: Thomas KELLER
Laura GUASCO

Local contacts: Anton DEVISHVILI

Samples: La1-xSrxMnO3, x=0.45, 0.5, 0.55, 0.6

Instrument	Requested days	Allocated days	From	To
SUPERADAM	9	4	11/04/2023	15/04/2023

Abstract:

The modification of thin films and interfaces through hydrogenation is a flourishing field of research that has shown broad possibilities in tuning the physical properties of different systems. Much research recently has been conducted on correlated oxides, where hydrogen induced reversible metal-to-insulator transitions have been uncovered in different systems, such as as rare earth nickelates [1] and manganites. Regarding manganites, the majority of research focused on optimally doped LSMO(x=0.33) [2,3], and have shown a reduced average Mn oxidation state after hydrogenation, which affects the double-exchange interactions and the related ferromagnetism. This reduction mechanism is the equivalent to that of electron doping [4]. By starting from an overdoped Sr-concentration we hence expect to be able to switch across different magnetic phases, from AF to FM, by hydrogen exposure.
The aim of the proposed experiment is two-fold: tracking depth dependent magnetic profiles during in situ H exposure, while simultaneously studying the induced structural modifications of LSMO films at room temperature, which have not yet been studied.

Experimental report on proposal 5-54-385

Dates: 8.07.2021-13.07.2021

Experimental team: L. Guasco (MPI FKF), A. Devishvili (local contact).

Samples of composition Pd(5nm)/ $La_{1-x}Sr_xMnO_3$ (20nm) with x=0.45, 0.5, 0.55 and 0.6 were deposited by MBE on LSAT substrates of area 10 x 10 mm^2 (Fig.1). This doping range was chosen because of the vicinity between FM and AF phases in the bulk phase diagram. The LSMO was epitaxial, as confirmed by XRD and RHEED characterization. The thin palladium on the surface serves as catalyst for hydrogen molecule splitting. All samples were cut in 2 parts of equal area after the growth, which served as pristine and hydrogenation sample. All samples were characterized as well by SQUID magnetometry and magnetotransport measurements.

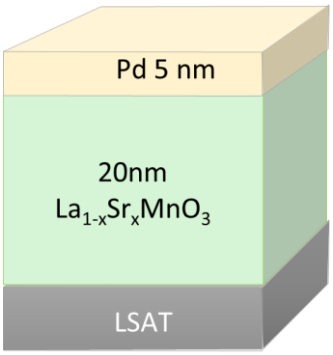

Figure 1: a. Sketch of single layer film of composition $La_{1-x}Sr_xMnO_3$

For this experiment we used in situ PNR during D_2 exposure of overdoped LSMO films (0.45<x<0.6) at room temperature. The deuterium gas was chosen in order to distinguish between oxygen depletion (which results in a decrease of LSMO scattering length density) and hydrogen incorporation (which in case of deuterium results in an increase of SLD), since these are the two expected results of H-exposure of manganite films. By using in situ resistivity measurement, we tracked the exposure process in an indirect way. The samples were kept in the deuterium atmosphere for several hours before reaching an equilibrium state. After that, the D_2 was replaced by helium atmosphere to allow the cooling down to cryogenic temperature. The use of PNR allows at the same time the detection of hydrogen absorption/ oxygen depletion as well as possible magnetic transitions.

This experiment was the continuation of a preliminary measurement performed previously at SuperADAM. In the previous experiment, the samples were exposed to D_2 gas ex situ, and after circa 14 days in air PNR was measured. Fig.2a shows the spin asymmetry defined as the difference between the down-down and up-up neutron reflectivities divided by their sum. This is a good indication of the in-plane component of the sample magnetization. From this quantity we can deduce a sizeable change in magnetic properties, with an average increase of the magnetic moment in the deuterated sample.

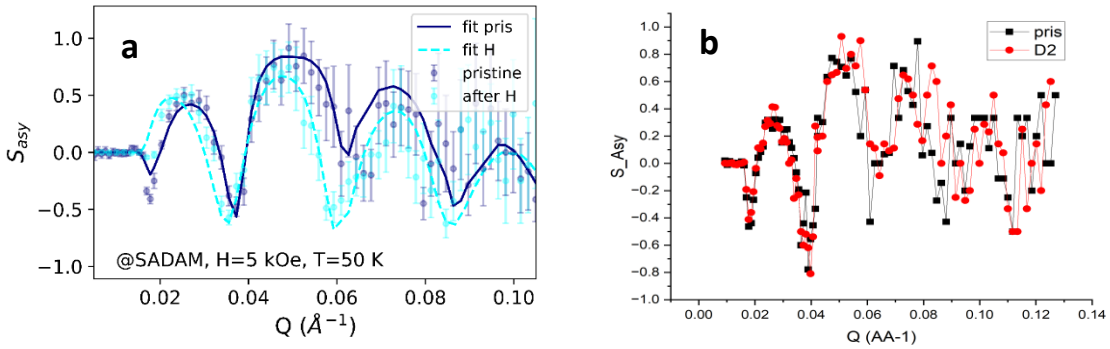

Figure 2: Low temperature spin asymmetry comparison of hydrogen exposed LSMO film with x=0.5 **a**. Spin asymmetry comparison of pristine and ex situ hydrogen exposed thin film after 2 weeks in air. **b**. Spin asymmetry comparison of pristine and in situ hydrogen exposed samples.

When the experiment was repeated with in situ exposure to deuterium gas, much smaller changes in the magnetic properties were observed (Fig.2b). This suggested that the exposure to air has an important role in the change of magnetic properties, for example through ion exchange mechanisms.

Nevertheless, a small change can already be observed without exposing the samples to air, as the fitting to model profiles suggested. Figure 3 shows an example for the sample with doping x=0.55 at 10 K: the nuclear depth profile mostly reveals changes in the Pd capping layer, while the magnetic profile shows a higher average magnetization after D_2 exposure.

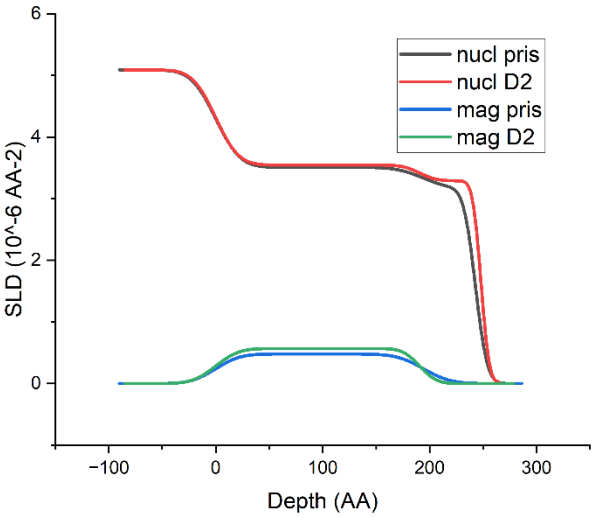

Figure 3: SLD depth profile of sample x=0.55 before and after exposure to deuterium gas.

The unchanged nuclear profile suggests no hydrogen incorporation, however this could also be compatible with a simultaneous deuterium incorporation and oxygen depletion, which was previously observed in similar complex oxide systems. A follow up experiment with H_2 gas could give more insight about this process.