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Local scale ordering in $LaMnO_3$ under pressure: x-ray absorption study

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Abstract. The present study aims, by using X-ray Absorption Spectroscopy, to describe the local process towards the pressure-induced abrupt changes in the resistivity in the Jahn-Teller distorted $LaMnO_3$ doped compounds. Local environment of manganese atoms under pressure up to 37 GPa has been studied by X-ray absorption spectroscopy. We identify successive steps towards the pressure-induced abrupt changes in the resistivity. These steps are associated to local processes such as the opening of the inter-octahedra tilt angles and the average symmetrization of the Mn local environment. All modifications present a hysteretic behavior when the pressure is released, pointing to the coexistence of MnO_6 distorted and undistorted units.

1. Introduction

$LaMnO_3$ doped alloys are puzzling materials where the magnetic and transport properties can be drastically changed by subtle modifications in the chemical composition and external conditions. These changes are related to modification in the local order (octahedral distortion and tilting angle among adjacent octahedral) through delicate balance between charge trapping and hybridization. High pressure is an unique tool to tune the interplay between lattice and electronic degrees of freedom and to investigate the actual path from a given magnetic and transport state towards another one.

In $LaMnO_3$ every manganese ion has a nominal charge 3^+ and no hole doping exist. The ground state is well understood as an A-type antiferromagnetic insulator with orthorhombic structure, with long range ordered, Jahn-Teller (JT) distorted MnO_6 octahedra that have four shorter and two longer bonds. The elongated e_g orbitals lie down in the xy plane and alternate between pointing along the x and y directions. At ambient pressure the compound undergoes, at temperatures around $710-750\,K$, a transition to a nearly cubic phase accompanied by an abrupt change of resistivity, revealing a concomitant transition to a metallic state. The application of an external hydrostatic pressure reduces the transition temperature. The Insulator-to-Metal transition takes place at room temperature when the applied pressure is close to32 GPa [1]. From the structural point of view, the pressure produces a continuous reduction of the lattice

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distortions (i.e. of the cooperative JT distortion) and experimental studies by X-ray diffraction predicted a quenching of the local JT splitting around 18 GPa. On the other hand ab initio calculations indicate that the stabilization of an insulating state under pressure in $LaMnO_3$ requires Jahn-Teller distortions in addition to on site Coulomb repulsion [2, 3].

Although the use of X-ray absorption spectroscopy (XAS) has been conclusive to elucidate many critical points of the local structure of $LaMnO_3$ and its doped alloys [4], few pressure dependent XAS measurements have been performed yet. This is in part related to inherent experimental difficulties in the collection of the XAS high pressures data at the Mn K-edge, arising both from the low transmission of the diamond cells and from the strong additional absorption due to the La L-edges. These difficulties are now overcome by the use of partially or fully perforated diamonds.

2. Experiments and methodology

Ceramic polycrystalline samples of $LaMnO_{3.00}$ were prepared by the nitrate method from high purity oxides, as described in Ref. [5]. Oxygen stoichiometry is carefully controlled through a final heat treatment under partial oxygen pressure. The XAS measurement have been performed at the Mn K-edge (6539 eV) at LUCIA beamline [6] hosted at the Swiss Light Source synchrotron facility. The beam is monochromatized with a Si(111) crystal and focused to a 5x5 μm^2 spot (FWHM) in a diamond anvil pressure cell, using a pair of mirrors in a Kirpatrick-Baez (KB) geometry. In order to limit the absorption of the anvil cell, we have used fully perforated diamond anvils supporting 500 μm thick mini diamonds. The culet of the mini diamonds was 200 μm. Silicon oil has served as a pressure-transmitting medium. Throughout the experiment the KB system provided a high and stable flux and beam position. The beam intensity was stable within about 5% and energy by less than 0.05 eV. The measurements were performed at room temperature, from ambient pressure to 37 GPa at regular steps of the pressure increase and release. The pressure in the cell was measured through the line shift of luminescence ruby with an accuracy of the order of a fraction of GPa. The incident energy was calibrated at the K-edge absorption inflexion point of Mn metal foil. The overall resolution, including experimental part and core level width, was about 2 eV. The reproducibility of the XANES features were checked before and after a 20 hours long experiment from ambient pressure up to 37 GPa and down to ambient. The edge position was recovered within 0.1 eV. The data have been collected with good signal over noise ratio and are Bragg peak-free up to about 250 eV above the energy threshold, allowing EXAFS data analysis up to kmax around 8 $\AA^{-1}$. The energy domain from 6535 eV up to 6556 eV has been scanned with energy step of 0.25 eV, to allow a detailed description of the preedge and the white line. We also used *ab initio* calculations to support the interpretation of the modification of XANES and pre-edge features as a function of pressure.

3. Results and Discussion

Figure 1 shows the XANES spectra collected for selected increasing pressures. All features of the spectra are in agreement with previously reported Mn K-edge data of $LaMnO_3$ at ambient conditions: two weak structures in the pre-edge region (6539-6543 eV), a shoulder A (6545-6552 eV) and an intense main peak B (also referred as white line) attributed to transitions from Mn $1s$ to Mn $4p$ levels, and a feature C resulting from multiple scattering contributions of MnO_6 surrounded by eight La atoms. The features A, B and C show subtle but significant modifications all over the pressure range.

The shift towards higher energy of the rising edge with increasing pressure is related to bond length shortening. Different regimes of compression can also be distinguished from the non-monotonous shift of the absorption edge (Fig. 2). At 32 GPa the total energy shift is about 1.5 eV, in reasonable agreement with the value of 2 eV estimated from a previous experiments [7].

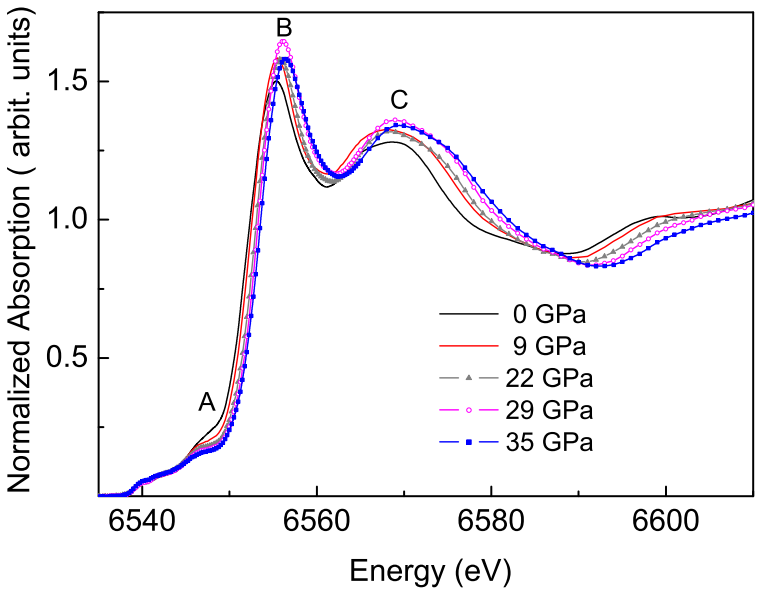

Figure 1. Evolution of XANES features at the Mn K-edge of $LaMnO_3$ for increasing pressure. The features A, B and C are described in the text.

When the pressure is released down to ambient, a hysteresis is observed from 26 GPa to around 7 GPa.

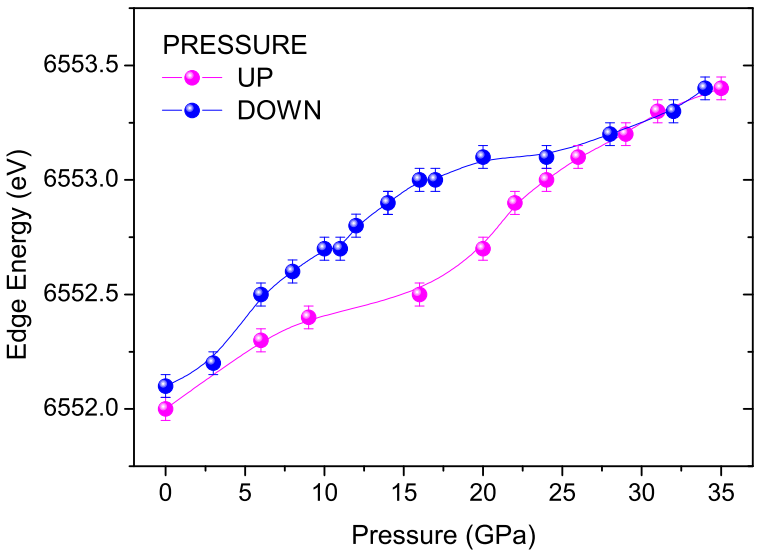

Figure 2. Mn K-edge energy, measured as the maximum of the first derivative, as function of the applied pressure for $LaMnO_3$. The edge energy evolution is related to the different regimes of compression. A hysteresis loop opens from 26 GPa down to 7 GPa.

The k-weighted χ(k) EXAFS spectra $[\chi(k) * k]$ for selected pressures are shown in figure 3. The amplitude of the EXAFS oscillations increase with pressure, as expected for a lower disorder. At the same time, a progressive shift of these oscillations account for the average shortening of the bonds. The Fourier Transform of the signal (Figure 4a) shows a main peak of oxygen first

neighbors (0.7 to 1.8 Å^{-1}), then a group (2.0 to 3.8 Å^{-1}) including single scattering of Mn and La neighbors and some dominant multiple scattering MS contributions [8].

The peak of oxygen neigbors is normally analysed with two contributions (1.94/2.15 Å), to take into account the Jahn-Teller distortion within the MnO_6octahedra. These two contributions merge totally here due to the limited k range (low resolution data). The area of this first peak is then directly related to the overall disorder of the coordination shell, including the Jahn-Teller splitting. The non-homogeneous increase of this area (Figure 4b), indicates a sequencial evolution in the local order. After a first compression regime ($<$ 9 GPa), followed by a plateau (9 to 16 GPa), the area strongly and monotonously increase up to a pressure around 26 GPa.This last pressure domain is probably associated to symmetrization of the MnO_6 octahedra [9]. Eventually, a regime of lower evolution takes place above 26 GPa up to the maximum value reached in the experiment.

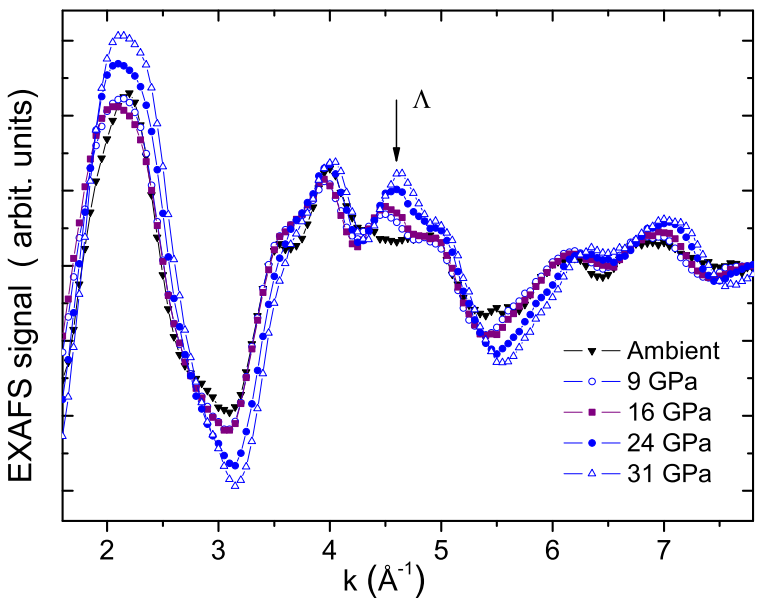

Figure 3. Evolution of EXAFS spectra at the Mn K edge of $LaMnO_3$ for increasing pressure.

Despite the restricted k-space available relevant information can be derived on the distortions of the MnO_6octahedron from EXAFS data fitting. Relative Debye Waller (DW) parameters, taking with reference to the DW parameters in the sample at 37 GPa, are reported in figure 4b. We should note that the result of the fitting procedure should be handled with some care as the quality of the fits strongly varies with pressure. That is, besides for the data collected at the highest pressures - with the most symmetric octahedra- the DW parameters resulting from the fitting procedure may include systematic errors whose amplitude is not constant. This systematic errors will also be correlated to the global evolution of the structure. The error bar given on the figure is only an estimated mean value. However it is clear that the increase of the integral and the decrease in the Debye-Waller parameters are strongly correlated. Both account for an improvement in the organisation of oxygen atoms around Mn with increasing pressure.

When the pressure is released down to ambient, a hysteresis is observed from 26 GPa to 7 GPa, as it is also observed for all XANES features. Such hysteresis suggests the occurrence of a mixture of phases with close compositions and related structures[10]. The present data may then be examined considering that application of the pressure above a threshold value would induce the progressive formation of MnO_6 undistorted units coupled to distorted ones. The coexistence of distorted and undistorted octahedra may account for the hysteretic behavior.

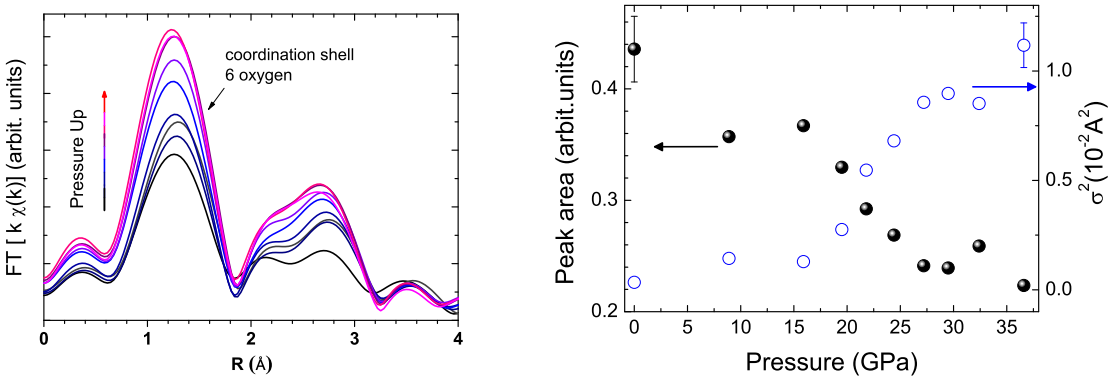

Figure 4. (a) Fourier transform of the k-weighted EXAFS spectra at the Mn K-edge of $LaMnO_3$ for increasing pressure. (b) Evolution of the structural disorder within the coordination shell, followed from the integral of this first peak (open dots, right scale) and from the value of the Debye-Waller parameter (full dots, left scale). The increase of the integral, as well as the decrease in the Debye-Waller parameter, are related to a improvement of the organisation of oxygen atoms around Mn.

We would like to call attention to the emergence of an additional EXAFS feature Λ at $k = 4.7$ Å^{-1} (Fig.3) at a pressure around 7 GPa. The feature Λ is common, with different scale of intensities, to all reported EXAFS spectra of manganite doped alloys compounds, but is absent in $LaMnO_3$ under ambient conditions. The origin of this feature is not perfectly determined. Following the recent work on the compared local structure in $LaMnO_3$ and $CaMnO_3$ [8] it can be related to multiple excitation effects. However the growth of this feature in $LaMnO_3$ with temperature or pressure motivates an interpretation in terms of a multiple scattering effect, closer to that we proposed for the thermal evolution of $LaMnO_3$ [11]. This additional contribution should be mainly due to MS paths involving two neighboring Mn atoms and their common oxygen [11]. The enhancement of the MS contribution is then likely related to a reduction of the average superexchange angle (tilt angle) $Mn - O - Mn$, (opening of the inter-octahedra tilt angles) and compatible with the formation of symmetric units. The threshold pressure of 7 GPa has already been identified in precedent studies [12, 1], as a breakpoint with anomalies in a and c lattice parameters and marked changes in compressibility. The authors associated these changes to the onset of the formation of MnO_6 undistorted units.This is in agreement with the present results on the disorder in the coordination shell.

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