ESRF	**Experiment title:** Disentangling Jahn-Teller cooperative distortion in $RMnO_3$ (R = Pr, Sm, Tb, Dy) at high pressures by X-Ray Absorption Spectroscopy	**Experiment number**: HC-3040
Beamline: BM23	**Date of experiment**: from: 15th juin to: 20th juin	**Date of report**: 18/08/2017
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Report:

Rare-earth manganites ($RMnO_3$) are outstanding compounds as they exhibit a huge panoply of physical properties arising from the intimate interplay between lattice, spin, orbital and electronic degrees of freedom.[1] It has been demonstrated that the physical behavior of these materials can be rather understood on the basis of MnO_6 octahedra rotations and cooperative Jahn-Teller distortion (JTD) underlying the P*nma* symmetry, common to these systems.[2] Hydrostatic pressure has been found as an important external parameter that by modifying the interatomic distances allows tuning the interactions to a much larger extent that any other external parameter.[3,4] In this report, we summarize the results obtained in the first high-pressure studies done at BM23 beamline, whose success in measuring the Mn K-edge of $GdMnO_3$ allowed expanding the experimental capabilities of this beamline. The expected main objectives of this experiment were: i)unravelling the pressure dependence of the JTD and to check its presumable persistence at high pressure; (ii) study the role played by the JTD for the mechanism of the insulator-to-metal phase transition.

In this experiment, we have focused on the K-edge of the Mn cation (energy: 6.5 keV). To reach high hydrostatic pressure, we have used two minianvils: one partially perfurated while the other completely perfurated. The pressure transmitiing medium was a mixture of ethanol and water. We have analysed the X-ray absorption in the 6.400 – 7.088 keV energy range. The χ^*k^2 EXAFS spectra taken under different fixed pressures are plotted in Figure 1(a), and the result from averaging a sufficient number of differences between the two conventional EXAFS spectra obtained at the same pressure was fitted (example in Figure 1(b)).

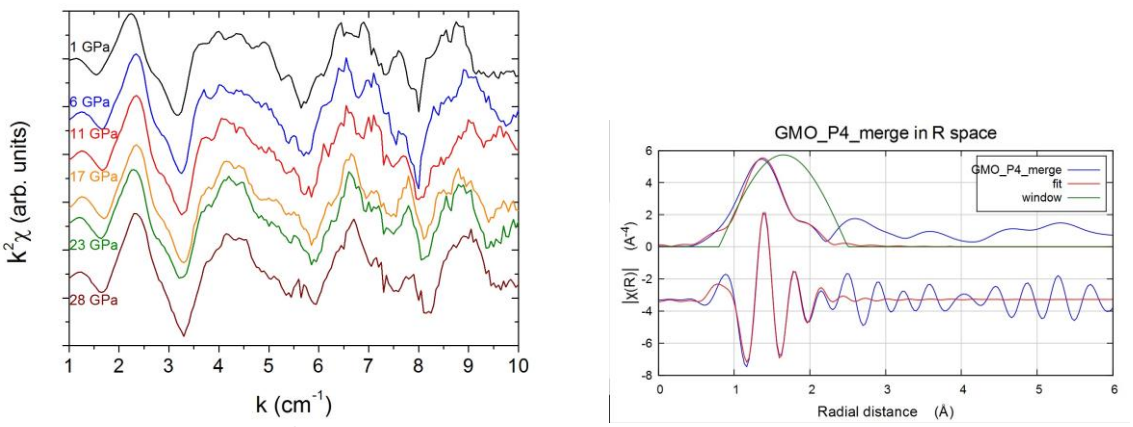
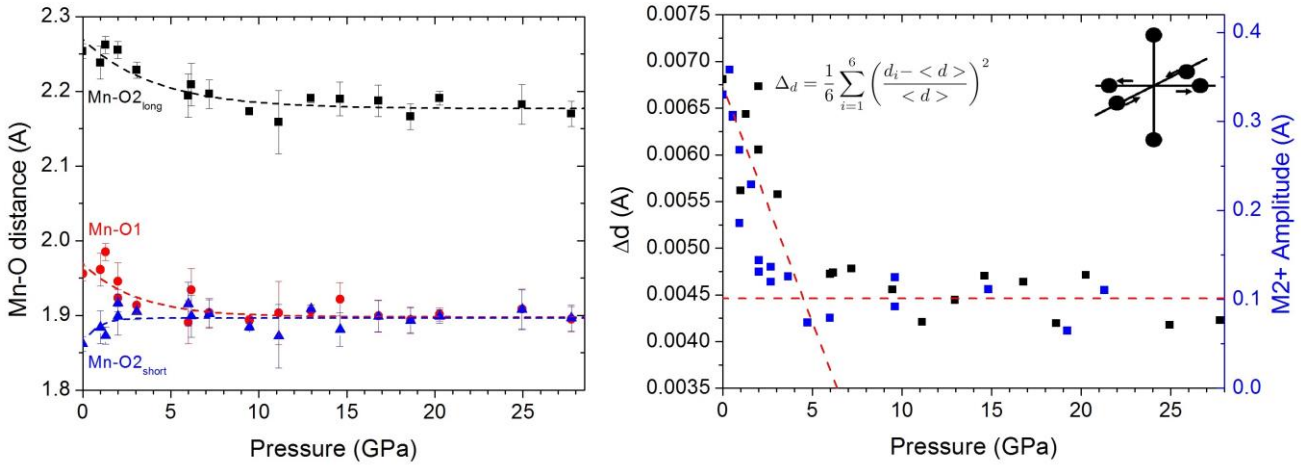


Figure 1. (a) $GdMnO_3$ χ^*k^2 EXAFS signal recorded at different fixed pressures. (b) Example of signal and fit from χ^*k^2 EXAFS signal for the spectrum taken at 9.5 GPa.

Changes on the oscillation maximum position aroud arround 2 A^{-1} are detected just above 6 GPa, and on the oscillation patterns in the 3.5-6 A^{-1} range, above 17 GPa (see Figure 1). The interpretation of these changes could be better studied by the data analysis, performed using Artemis within Feff 8 calculations. The average spectra were analysed considering a local distortion for MnO_6 ostahedra using 3 different average distances with N = 3, and only one Debye Waller factor for different types of paths. An example of such a fit for shells up to R = 1 A is shown on figure 2, being S02 fixed to 0.7.



(a) (b)

Figure 3: Pressure dependence of: (a) the Mn-O bond lengths obtained from the analysis of the EXAFS data; (b) the M2+ amplimode and the disotrion parameter Δd. The inset shows the motion involved in the M2+ amplimode.

Figure 3(a) shows the pressure dependence of the Mn-O bond lengths determined by EXAFS analysis. The pressure dependence of the Mn K-edge EXAFS on $GdMnO_3$ (up to 30 GPa) revealed an unexpected result: the JTD is strongly reduced and eventually suppressed above 5 GPa. As an alternative way to get insight into the structure evolution, we performed a symmetry-mode decomposition of the P*nma* structures with respect to the Pm-3m parent structure using the Amplimodes tool of the Bilbao Crystallographic Server. This enables to identify the structural properties and theirs strengths as a fucntion of pressure, using the XRD data, already obtained in last experiments in ID27. There is an excelent scalling between the M2+ amplimode associated with the MnO_6 octahedron distortion with the distortion parameter Δd, as it can be ascertained from Fig. 3(b). The results already obtained point clearly for the existence of an unknown intermediate isostructural phase transition occurring at pressures well below the critical pressure of the insulator-metal phase transition (52 GPa), and rises the question if this is a universal behavior of orthorhombic $RMnO_3$ under pressure. Ongoing analysis of the second shell is running in order to get information regarding other structural deformations.

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