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Trevor A. Tyson, Department of Physics, New Jersey Institute of Technology tyson@adm.njit.edu

Pressure Induced Atomic Structure Transformations in Manganites

Congwu Cui,¹ Trevor A. Tyson,¹ Zhong Zhong,² Jeremy P. Carlo,¹ and Yuhai Qin¹

¹ Physics Department, New Jersey Institute of Technology, Newark, NJ

² National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY

The evolution of the atomic structure of the manganite $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$ under pressure was explored through high-pressure x-ray powder diffraction measurements. It is shown that an atomic structure transformation occurs between ~2-4 GPa, in which the Jahn-Teller distortion (JTD) of the MnO_6 octahedra is enhanced, in parallel with an increase in the Mn-O1-Mn bond angle. Above ~4 GPa, the Mn-O1-Mn bond angle is reduced with the JTD remaining unchanged. These structural measurements enable a better understanding of the electrical, magnetic, and the metal-insulator transition behavior in manganites under pressure.

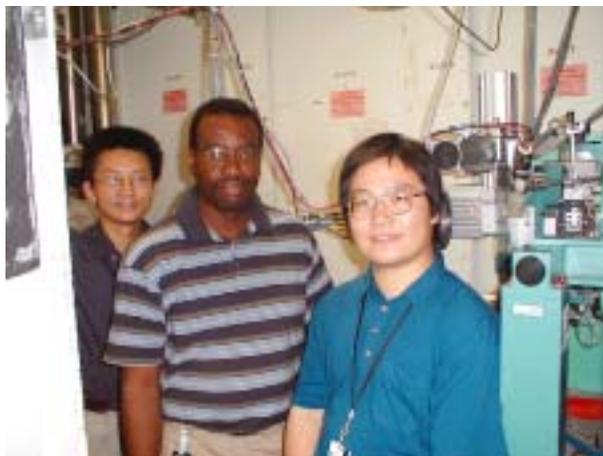
The atomic structure of the MnO_6 octahedra plays an important role in manganite systems of $Ln_{1-x}A_xMnO_3$ ($Ln = La, Pr, Nd, \text{ etc.}; A = Ca, Sr, \text{ etc.}$) with colossal magnetoresistance. Pressure has been used to modify the lattice and various bulk properties. Below ~2 GPa, it is argued that pressure enhances the ferromagnetic metallic state in the $La_{1-x}A_xMnO_3$ system ($A = Ca, Sr, \text{ and } x \sim 0.2-0.5$) by compressing the lattice constants, increasing the Mn-O-Mn bond angle, making the unit cell more cubic and hence reducing the local distortion of the MnO_6 octahedra and electron-lattice coupling. In this range pressure effects are similar to and can be scaled to those of chemical doping. In our work, we have found that this is not true at higher pressures.

$La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$, the system studied, is a typical manganite system with a very high magnetoresistance of ~10000% at 6 T and a Curie temperature T_C and metal-insulator transition temperature T_{MI} coincide at ~150 K. In this material, there ex-

ist strong electron-lattice and spin-lattice coupling. Our high-pressure electron transport measurements indicate that pressure increases T_{MI} and conductivity below $P^* \sim 3.8$ GPa, but T_{MI} and conductivity decrease quickly with pressures above P^* . The conductivity in the range of liquid nitrogen to room temperature and the localization length due to spin disorder in the paramagnetic phase follow the same trend as T_{MI} . This possibly suggests a pressure induced crystal structure change (local-long range).

To understand the changes in atomic structure with pressure, high-pressure powder x-ray diffraction measurements with a diamond anvil cell were carried-out. It is found that pressure induces a structural transformation within the MnO_6 octahedra in the range ~2-4 GPa, in which the Jahn-Teller distortion (JTD) is enhanced and the MnO_6 octahedra align. Above this range, the JTD is stable, but the MnO_6 octahedra buckle as in the low pressure regime (**Figure 1**).

The diffraction patterns were refined with the Rietveld method on the basis of the 1 atm Pbnm space group. While the unit cell is compressed (**Figure 2a**), the Mn-O bond length and Mn-O-Mn bond angle change with pressure in a complicated manner (**Figure 2b and 2c**). Below ~2 GPa, all three Mn-O bonds are compressed and the bond angles are unchanged. This may explain the T_{MI} and resistivity behavior. According to the double exchange theory: the overlap of $Mn^{3+} e_g$ and $O^{2-} 2p$ band and hence the hopping integral is increased due to the Mn-O bond compression. From ~2 to ~3 GPa, the splitting of



Authors (from right): Congwu Cui, Trevor A. Tyson, and Zhong Zhong.

the two in-plane Mn-O2 bonds increases, hence the coherent Jahn-Teller distortion,

$$\delta_{JT} = \sqrt{\frac{1}{N} \sum (R_{Mn-O} - \langle R_{Mn-O} \rangle)^2}$$

increases abruptly (**Figure 2d**); the Mn-O1-Mn bond angle increases by $\sim 20^\circ$ while the Mn-O2-Mn bond angle decreases slightly. The competing mechanisms of increasing JTD and bond angle may lead to the saturation of T_{MI} and resistivity at P^* . Above ~ 4 GPa, the

JTD is stabilized, the Mn-O1-Mn bond angle, characterizing the tilting of MnO_6 octahedra, drops with pressure. The overlap of the O^{2-} 2p orbital and the Mn^{3+} e_g orbital decreases and the charge carriers are more localized with further pressure increases. Therefore, reversed metal-insulator, resistivity, and magnetic behavior occur.

Transport studies reveal pressure-induced distortions of the MnO_6 octahedra in the whole class of the

colossal magnetoresistive materials with varying bandwidth. The identification of the structural changes under pressure may lead to a better understanding of the physics of these materials.

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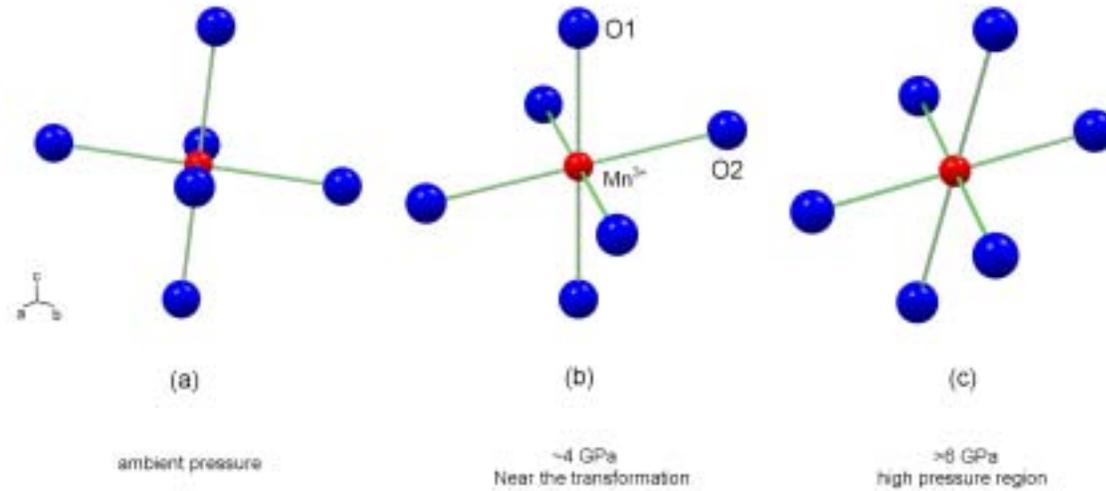


Figure 1. The Jahn-Teller distortion and tilting of the MnO_6 octahedra under pressure in $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$.

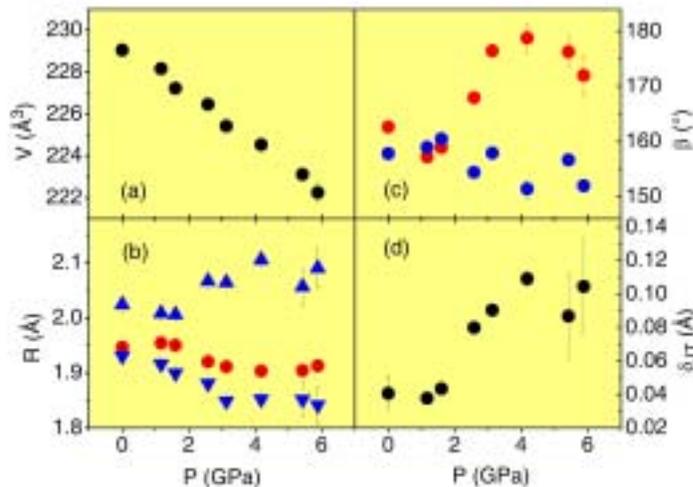


Figure 2. Pressure dependence of structure parameters of $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$ at room temperature. (a) Unit cell volume; (b) Mn-O bond lengths of the “ab-plane” Mn-O2 bonds (up and down solid triangles) and “c-axis” Mn-O1 bond (circles); (c) The “ab-plane” Mn-O2-Mn (blue circles) and “c-axis” Mn-O1-Mn (red circles) bond angles; (d) The coherent Jahn-Teller distortion parameter, defined as

$$\delta_{JT} = \sqrt{\frac{1}{N} \sum (R_{Mn-O} - \langle R_{Mn-O} \rangle)^2}$$