A NEW INTERPRETATION OF THE CO STATE IN HALF-DOPED MANGANITES: THE ORDERING OF ZENER POLARONS.

A. Daoud-Aladine [1], J. Rodríguez-Carvajal[1], L. Pinsard-Gaudart[1,2], M.T. Fernández-Díaz[3], A. Revcolevschi[2].

[1]Laboratoire Léon Brillouin (CEA-CNRS), CEA-Saclay, 91191 Gif sur Yvette, France.
[2]Laboratoire de Physico-Chimie des Solides, 91405 Orsay, France
[3]Institute Laue-Langevin, 38042 Grenoble, France

The calcium-doped manganites $R_{1-x}Ca_xMnO_3$ (x~0.5) (R: rare-earth) are known to display a structural phase transition at T_{CO}. This transition is usually attributed to charge and orbital ordering (CO/OO) because it is associated with a jump of the resistivity and to the onset of superstructure reflections in the low temperature (LT) phase. Moreover their complex spin ordering, at a temperature $T_N < T_{CO}$, has been traditionally interpreted by using the semi-empirical Goodenough-Kanamori-Anderson rules for the superexchange interactions. These rules have been applied to a model of Mn^{3+} d_{z^2} orbital ordering in the (**a**, **b**) plane, proposed in the late fifties by Goodenough [1]. The fact that this model suggests a charge ordered pattern of Mn^{3+} and Mn^{4+} ions, has promoted the idea that the magneto-transport properties of these compounds are strongly influenced by dynamic CO/OO driven by the combined effect of Coulomb repulsion and Jahn-Teller distortion around the Mn^{3+} sites. It is expected that CO will result in the setting up of MnO_6 octahedra of different average Mn-O distances ($\langle d_{Mn-O} \rangle$). The experimental determination of these displacements has been attempted on $La_{1/2}Ca_{1/2}MnO_3$ by neutron and synchrotron powder diffraction [2] making use of *a priori* constraints, and symmetry, according to the pattern shown in Figure 1(left).

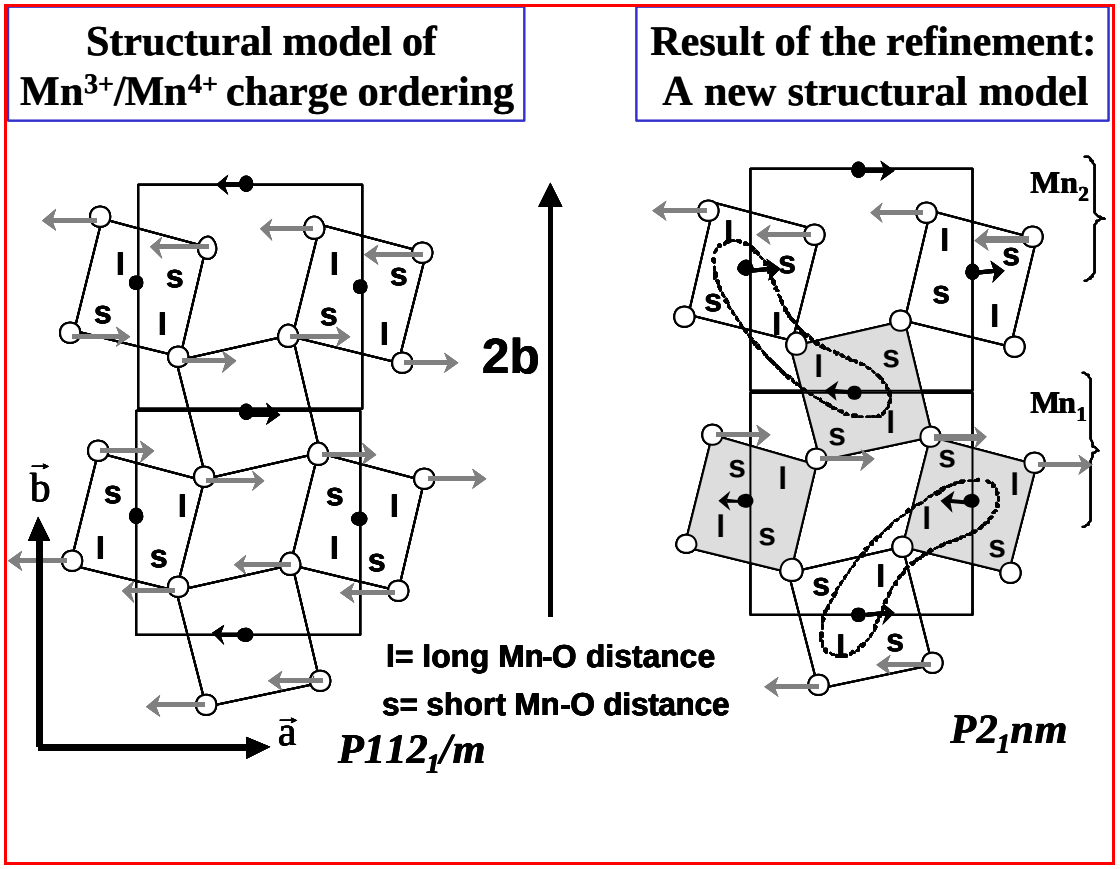

Figure 1. (left) Schematic atomic displacements of the conventional Mn^{3+}/Mn^{4+} model for the CO in half doped manganites with respect to the high temperature phase, (right) experimentally determined pattern of atomic displacement. The amplitude of displacements, represented by arrows, is exaggerated for clarity.

We have performed a neutron diffraction experiment on a single crystal of $Pr_{0.6}Ca_{0.4}MnO_3$ [3] that has provided a quite different picture of the displacement pattern (see Figure 1(right)). Instead of the distortion pattern expected for the CO/OO picture the two non-equivalent MnO_6 octahedra have similar $\langle d_{Mn-O} \rangle$. There is also an off centering of the Mn ions resulting from the loss of the inversion center at the Mn sites. These structural details are inconsistent with the picture of Mn^{3+}/Mn^{4+} charge ordering. The persistence of mixed valence state of Mn atoms in the LT phase is confirmed by the nearly equal $\langle d_{Mn-O} \rangle$ on the two sites. This result is totally in agreement with previous XANES studies that have already mentioned a unique intermediate valence state displayed by half-doped manganites across the CO/OO transition.

The analysis of the atom displacements indicates that the Mn_1-O_3-Mn_2 angle is the most opened angle in the LT structure. The elongation of the octahedra further suggests that one electron is shared by the $Mn_1(e_g)$-$O_3(2p)$-$Mn_2(e_g)$ units, keeping the intermediate valence of both Mn atoms. This is consistent with Mn_1-Mn_2 pairs coupled via a local double exchange (DE) process mediated by the O_3 oxygen, corresponding to the image of a Zener polaron. The electronic localization below T_{CO}, in these compounds, can be then explained by a partial localization of the electrons beyond the atomic limit. This interpretation of the structural distortions suggests the appearance, below T_{CO}, of ordered Mn_1-O_3-Mn_2 molecular objects (Zener polarons) with ferromagnetically coupled Mn moments (see Fig. 2). This hypothesis gives also a clue to interpret the anomaly in the magnetic susceptibility observed at the, supposedly purely structural, transition for compounds that remain in a paramagnetic state below T_{CO} [3]. The formation of Zener polarons leads to new elemental paramagnetic units with a higher effective moment. The extension of this image to other compounds of the manganites family is being investigated. In particular the CO in $La_{1/3}Ca_{2/3}MnO_3$ may be interpreted in terms of Zener polarons involving three Mn atoms.

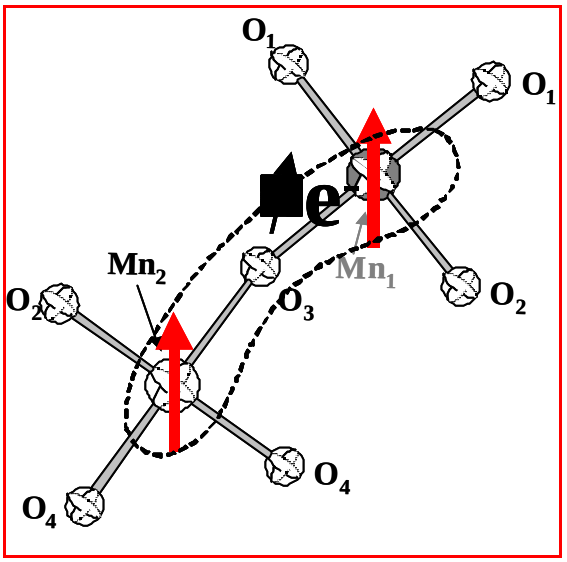

Figure 2. Schematic image of a Zener polaron

References

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[3] A. Daoud-Aladine, J. Rodríguez-Carvajal, L. Pinsard-Gaudart, M.T. Fernández-Díaz and A. Revcolevschi., Phys. Rev. Lett.**89** (2002) 097205