CRYSTAL AND MAGNETIC STRUCTURES OF THE Mn^{3+} ORBITAL ORDERED MANGANITE $Y_2Ba_2Mn_4O_{11}$

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The discovery of the colossal magnetoresistance in manganese oxide perovskites ($AMnO_3$) of general formula $R_{1-x}D_xMnO_3$ (R = trivalent rare earth cations, D = divalent cations like Ca, Sr, Ba, Pb…) [1] has recently attracted the focus of many research efforts, in order to understand and to improve their properties. By changing the D-cation and/or the doping level, one can tune their physical properties from ferromagnetic (F) conductors to antiferromagnetic (AF) insulators. For a large average radius of the A-site ($<r_A>$) the conduction band is broad and the material has, in general, a metallic-like behaviour. This is usually explained by the double exchange mechanism [2]. If $<r_A>$ is small enough the conduction band is narrow, leading to a localization of the charge carriers on specific atomic sites. In some cases the localization occurs in a spatially ordered way. This phenomenon is called charge ordering (CO) and it is accompanied by an increase of the resistivity. Goodenough [3], using super-exchange theory, and stressing the role of the Jahn-Teller effect on Mn^{3+}, was the first to propose a model explaining qualitatively the magnetic structure of $LaMnO_3$. Combining these concepts with a specific charge and orbital ordering he was able to provide an explanation for the low temperature observations in half-doped (x=1/2) manganites. Recently, Daoud-Aladine *et al*. [4] have proposed an alternative model in which the electrons localize in regions formed by Mn-O-Mn ferromagnetic pairs (Zener polarons), which are stabilized by a local double exchange mechanism and a structural distortion. In order to test different hypotheses about the nature of the CO/OO transitions new compounds have to be studied in both mixed and integer valence materials. To overcome the disorder in the A-site of the Mn perovskites we are exploring new compounds presenting well ordered structures.

The first example of A-cation ordered manganese perovskite was $YBaMn_2O_5$ (Fig. 1), in which Y^{3+} and Ba^{2+} cations are ordered in alternating layers perpendicular to [001] and the oxygen sites in the Y-layer are empty. Neutron diffraction studies showed that $YBaMn_2O_5$ has a tetragonal symmetry [5] and a charge ordered arrangement of Mn^{2+} and Mn^{3+} ions. By low temperature oxygenation it is, in principle, possible to obtain mixed valence compounds of formula $YBaMn_2O_{5+\delta}$ so that it is expected to have Mn^{2+}/Mn^{3+} for $\delta<0.5$ and Mn^{3+}/Mn^{4+} for $\delta>0.5$. For $\delta=0.5$, we obtained a stoichiometric compound that can be formulated as $Y_2Ba_2Mn_4O_{11}$ or $YBaMn_2O_{5.5}$ and which have only Mn^{3+}.

The compound $YBaMn_2O_{5.5}$, has been prepared by oxidizing/reducing $YBaMn_2O_5/YBaMn_2O_6$ in mild conditions. We used the combined data of three independent diffraction patterns at room temperature: one X-ray and two neutron powder patterns to refine the structure. The crystal structure of this manganite was solved in the space
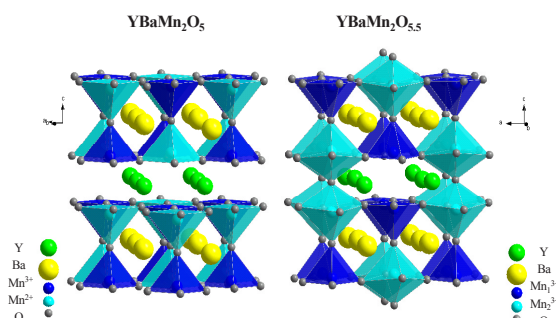

Figure 1. Perspective view of the $YBaMn_2O_5$ and $YBaMn_2O_{5.5}$ perovskites

group *Icma* ($a \approx 8.161$ Å, $b \approx 7.546$ Å, $c \approx 15.279$ Å) [6]. We have shown that a doubling of the cell is present in this case, as compared to the La-based compound [7], due to a tilting ($a^0b^0c^-$) of the polyhedra around the [001] direction. Even though the formal oxidation degree of manganese ions is 3+, in the structure there are two different sites: one with a square pyramidal coordination (Mn1) and another one with octahedral coordination (Mn2). In the *ab* plane, the structure consists of rows of MnO_6 octahedra and MnO_5 pyramids parallel to the *b* direction. In the *a* direction the rows are formed of alternating octahedra and pyramids and in the *c* direction the rows consists of alternating pairs of octahedra and pyramids following the site sequence 1-1-2-2-1-1-2-2. The

result of this stacking is the presence of tunnels along the **b** direction (Fig. 1). The existence of two distinct types of Mn^{3+} cations, in square pyramidal and octahedral coordination, leads to the formation of a particular orbital ordering.

We have also investigated its magnetic and transport properties. The resistivity measurements have shown an insulator-like activated behaviour with a low activated energy, comparable to that of $LaMnO_3$. Magnetic susceptibility shows an antiferromagnetic transition at a Néel temperature of $T_N \approx 140$ K. The neutron powder diffraction patterns of $YBaMn_2O_{5.5}$ obtained below the Néel temperature show the presence of magnetic reflections that can be indexed by using the propagation vector **k**=(0,0,0). The refinement of the magnetic structure, at 1.7 K, gives the best result with the $G_x+G'_x$ mode (the first term refers to octahedral and the second -primed- to pyramidal Mn^{3+} ions). This leads to a picture of the magnetic structure, identical to that of $LaBaMn_2O_{5.5}$ [7], as a network of parallel ferromagnetic spin-ladders (Fig. 2a). Each F spin ladder lies along the **a**-axis, in the (010) plane, and it is AF-connected along the **b** and **c** axes to the neighbouring one. In the (010) plane, half of the manganese ions of every ladder are connected to adjacent ladders by the Mn2-O-Mn2 AF pathway. Along the [010] direction, all the Mn ions of a ladder are AF-connected to the upper and lower ladders. At 1.7K, the magnetic moment of the two kinds of Mn^{3+} ions are slightly different, $3.5(1)\mu B$ for the pyramidal site and $3.7(1)$ μB for the octahedral site. The reduction with respect to the expected moment is due to a combination of covalence and zero-point fluctuations of the AF structure.
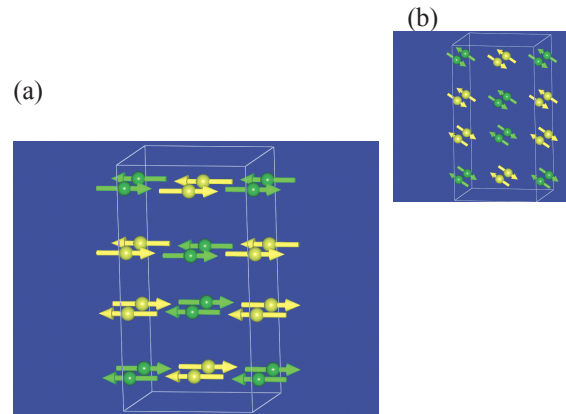

Figure 2. Magnetic structure of $YBaMn_2O_{5.5}$ at 1.5K (a) and 125K (b). Mn atoms in octahedral coordination are represented with black arrows. Mn atoms in pyramidal coordination are represented with grey arrows.

Moreover if we consider the magnetic interactions between the Mn^{3+} ions according to the orbital ordering deduced from the crystal structure we have shown that the analysis of the super-exchange paths, and the prediction of the signs of exchange interactions following the Goodenough-Kanamori-Anderson (GKA) rules is perfectly compatible with the observed magnetic structure.

Near the transition temperature (T~120K), a component along the **c**-axis must be taken into account in order to fit properly the neutron diffraction pattern (Fig. 2b). The presence of a single mode $(G_x+G'_x,0, G_z+G'_z)$ in both x and z directions implies a mixing of irreducible representations and this is a signature of the low magneto-crystalline anisotropy in this compound.

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