# Orbital State Study of Mn in Colossal Magnetoresistance Material $La_{2-2x}Sr_{1+2x}Mn_2O_7$ by Magnetic Compton Profile Measurement

Perovskite Mn oxides have been studied in relation to the colossal magnetoresistance (CMR) which is a huge decrease in electric resistance under a magnetic field. Recently, the double-layered manganite $La_{2-2x}Sr_{1+2x}Mn_2O_7$ has become of special interest, because it shows much larger CMR than the base compound $La_{1-x}Sr_xMnO_3$. As shown in Fig. 1, the crystal structure has a common feature in perovskite manganites that the Mn ion is octahedrally surrounded by O ions. In this crystal field, the energy levels of Mn 3*d* orbitals (which is 5-hold degenerated in a free atomic state) split into a triply degenerate $t_{2g}$ and a doubly degenerate $e_g$ states. When a hole is doped in this system, which is introduced by $Sr^{2+}$ ion doping, it goes into the $e_g$ orbital. That makes $e_g$ electrons hop around the Mn sites. The hopping also causes ferromagnetic alignment of the Mn spins through the strong Hund's coupling with localized $t_{2g}$ spins. This is what we call the double exchange (DE) mechanism. It can explain both the coexistence of metallic conduction and ferromagnetism in manganites [1]. However, recent experimental results have revealed that the magnitude of CMR and complicated magnetic phase diagrams cannot be explained only by the simple DE mechanism [2-4]. The importance of the orbital degree of freedom is pointed out as well as the charge and spin ones. This means that the populations of $x^2-y^2$ and $3z^2-r^2$ orbitals in the $e_g$ state play a key role in understanding the transport and magnetic properties of this system.

We have investigated the orbital state in $La_{2-2x}Sr_{1+2x}Mn_2O_7$ by magnetic Compton profile (MCP) measurement [5]. The MCP measurement has been used as a unique method to determine the electron-spin momentum density in ferromagnetic materials. In addition, it has the following advantages to define the orbital occupation; that is, MCP changes its shape depending on the orbital state occupied by magnetic electrons, and it also depends on the direction of the scattering vector of X-rays with respect to the crystalline axis. These features enable us to differentiate the electron population in $x^2-y^2$ and $3z^2-r^2$ orbitals together with $t_{2g}$ state through the measurement of MCP by using a single crystalline sample. Experiments have been made at beamline **BL08W** using circularly polarized X-rays of 270 keV. The MCP's were measured along [100], [110] and [001] directions for $La_{2-2x}Sr_{1+2x}Mn_2O_7$ with x = 0.35 and 0.42.

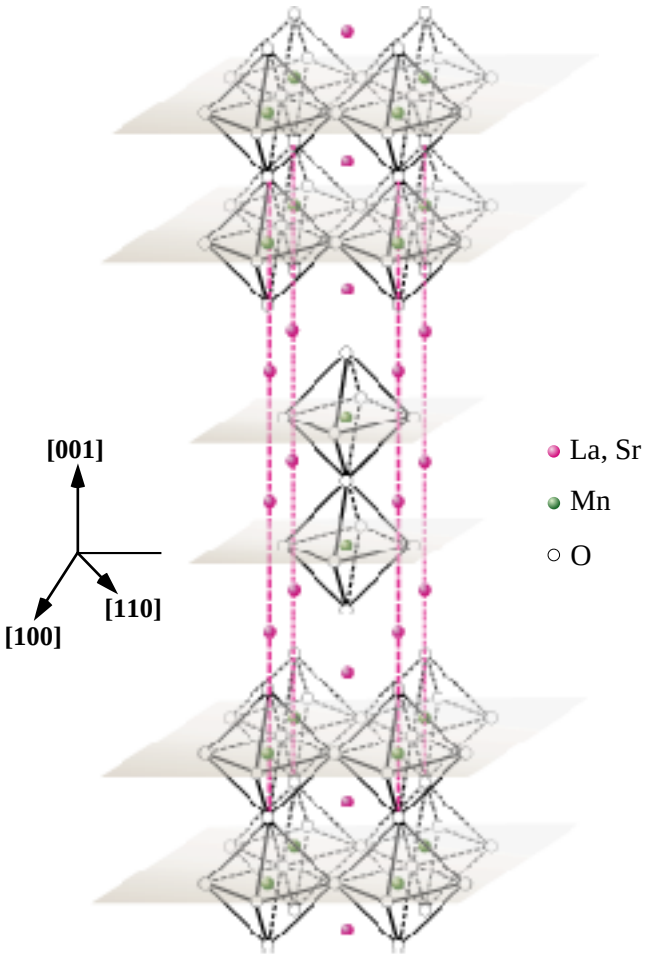


*Fig. 1. The crystal structure of $La_{2-2x}Sr_{1+2x}Mn_2O_7$.*

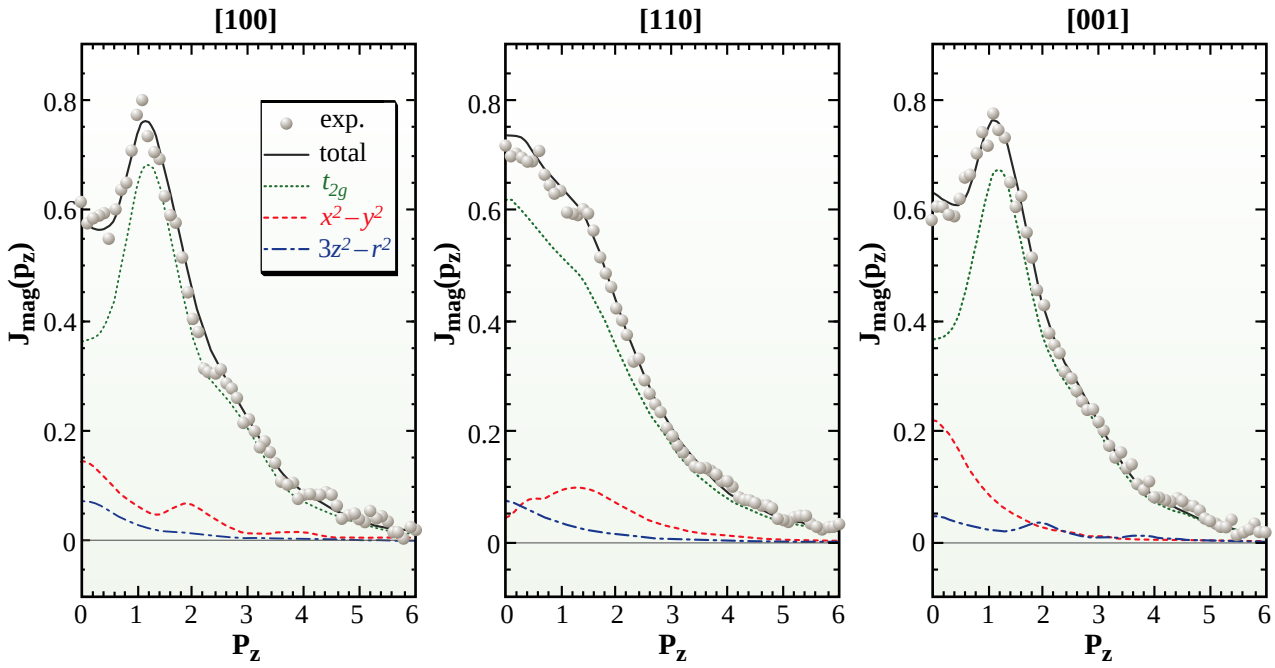


*Fig. 2. The magnetic Compton profiles along the [100], [110] and [001] directions in $La_{2-2x}Sr_{1+2x}Mn_2O_7$ with x = 0.35. Experimental data (solid circles) are shown with fit (solid gray line) using the $MnO_6$ cluster orbitals. Also shown are the $t_{2g}$ orbital (dotted green line), $x^2-y^2$ orbital (dashed red line) and $3z^2-r^2$ orbital (dash-dotted blue line) contributions.*

Figures 2 and 3 show respectively the MCP's of x = 0.35 and 0.42 samples obtained at 10 K. The clear anisotropy of MCP reflects the orbital state of magnetic electrons on Mn site. These MCP's were explained by theoretical Compton profiles obtained from an *ab initio* molecular orbital calculation for the $(MnO_6)^{8-}$ cluster which takes the hybridization effect between Mn 3*d* and O 2*p* orbitals into account. The theoretical analysis of the orbital state was made using these following conditions: Each MCP is normalized by the magnetic electron numbers per site estimated from the hole concentration *x*. The $t_{2g}$ occupation number is fixed to three per site because it is fully occupied. The remainder is fitted by the profiles of $x^2-y^2$ and $3z^2-r^2$ orbitals so that the area of fitted profile coincides with that of experimental one. The results are also shown in Fig. 2 and Fig. 3 with the dashed red line and dash-dotted blue line. Since the area of a profile is proportional to the number of electron spins in a state, the occupation numbers of $x^2-y^2$ and $3z^2-r^2$ orbitals can be thus obtained as 0.47 and 0.18 for x = 0.35 respectively, while they are 0.46 and 0.12 for x = 0.42. These results show that the $e_g$ orbital state is dominated by the $x^2-y^2$ -type orbital with almost constant occupation, while the occupation in $3z^2-r^2$ -type orbital decreases with the increase in the hole concentration *x*. This conclusion would explain the continuous change of magnetic structure from ferromagnetism via canted antiferromagnetism to A-type antiferromagnetism with an increase of *x*. The decrease of population in $3z^2-r^2$ orbital weakens the ferromagnetic coupling between $MnO_2$ layers through $e_g$ electron hopping. The superexchange coupling between $t_{2g}$ spins gradually overcomes the ferromagnetic coupling resulting in the antiferromagnetic structure at high *x* values.

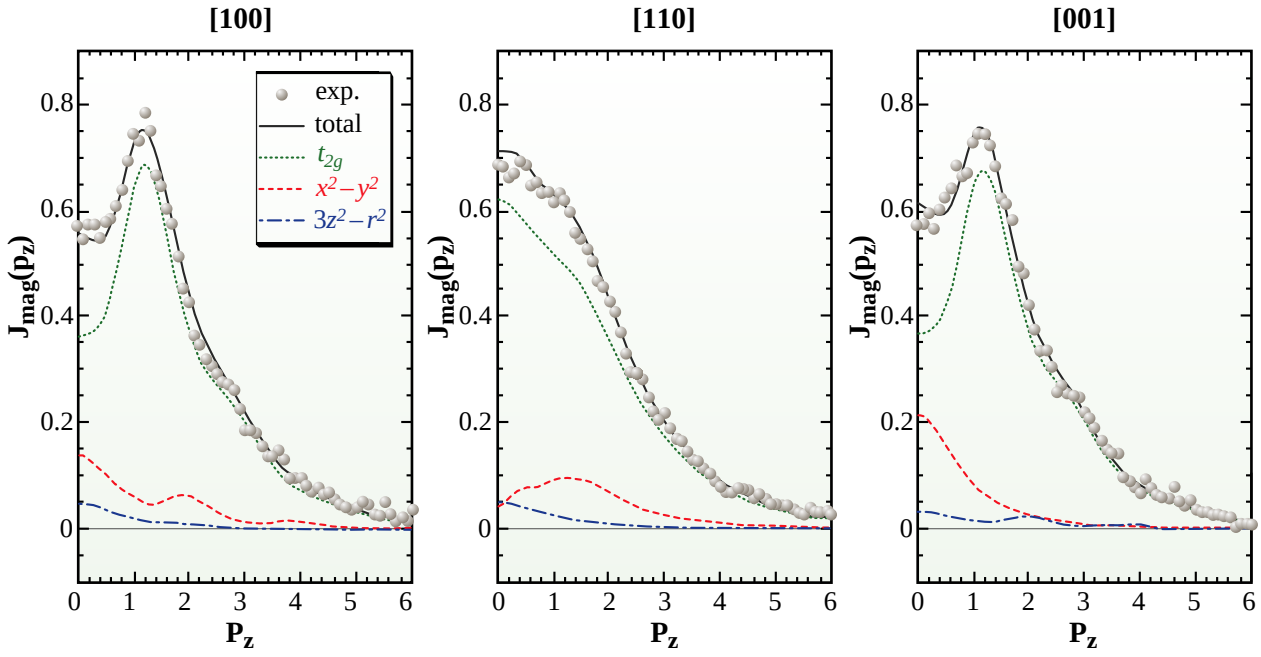


*Fig. 3. Same as Fig. 2 but for x = 0.42.*

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**References**

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