PHASE SEPARATION AND INSULATOR-METAL BEHAVIOR OF CMR MANGANITES

The doped manganites, $R_{1-x}Ca_xMnO_3$, where $R$ is a trivalent rare-earth metal, have a distorted-perovskite structure with three-dimensional networks of the MnO$_6$ octahedra. Their generic behavior of paramagnetic-to-ferromagnetic transition is understood within the framework of double-exchange theory. We need to consider additional effects in order to understand the insulator-metal behavior as well as the colossal magnetoresistance (CMR). At present, the most probable candidate is the percolation model [1], in which the insulator-metal behavior occurs when the percolation path of the metallic (ferromagnetic metallic; FM) is connected from one end to the other regions in the sea of the insulating (charge-ordered insulating; COI) state. The charge-ordering transition of doped manganites usually accompanies an antiferromagnetic transition with the CE-type structure, while the FM state is of half-metallic. Here, to judge the suitability of this model, we have performed a synchrotron radiation X-ray powder diffraction experiment on Nd$_{0.55}$(Sr$_{1-y}$Ca$_y$)$_{0.45}$MnO$_3$ at beamline BL02B2 with high angular resolution and counting statistics [2].

To choose an appropriate chemical composition for the present study, we first have synthesized a series of ceramics Nd$_{0.55}$(Sr$_{1-y}$Ca$_y$)$_{0.45}$MnO$_3$, finely controlling the one-electron bandwidth through chemical pressure. Powder X-ray diffraction measurements at room temperature along with Rietveld analysis indicate that the samples were single phase without detectable impurities. Figure 1 shows an electronic phase diagram of Nd$_{0.55}$(Sr$_{1-y}$Ca$_y$)$_{0.45}$MnO$_3$. The Curie temperature $T_C$ and the charge-ordering temperature $T_{CO}$ were determined from the temperature-variation of the magnetization $M$ and resistivity $\rho$. The insulator-metal behavior was enhanced in the proximity of FM-COI phase boundary (hatched region of Fig. 1). Thus, we have chosen Nd$_{0.55}$(Sr$_{0.17}$Ca$_{0.83}$)$_{0.45}$MnO$_3$ for present investigation. The inset shows magnetization curves measured at 10 K. The suppressed magnetization curve at 0.83 suggests a coexistence of the FM and antiferromagnetic COI phases [3].
In Fig. 2, we demonstrate prototypical examples of the X-ray powder diffraction patterns of Nd$_{0.55}$(Sr$_{0.17}$Ca$_{0.83}$)$_{0.45}$MnO$_3$ at 265 K and 110 K. At 110 K we observed remarkable splitting of the Bragg reflections, indicating the phase separation (see inset of Fig. 2(b)). We have analyzed the powder patterns below 200 K using a two-phase model with two distorted-perovskites (Pbnm; Z = 4). The Rietveld refinements are satisfactory, in which $R_{wp}$ and $R_I$ (reliable factor based on the integrated intensities) are fairly typical of published structures. These two perovskite phases can be characterized by a lattice constant $c$. Hereafter, we will refer to the respective phases as ‘short-$c’ (7.54 - 7.58 Å) and ‘long-$c’ (7.60 - 7.62 Å) phases.

Figure 3 shows temperature variation of (a) resistivity $\rho$, (b) lattice constants and (c) intensity of the magnetic Bragg reflections of Nd$_{0.55}$(Sr$_{0.17}$Ca$_{0.83}$)$_{0.45}$MnO$_3$. The most important point here is that the lattice constants indicate a discontinuous change at $T_{CO}$. In other words, the system is transformed into a two-phase state, both of which differ from the room temperature phase. Such a state is perhaps ascribed to the random nucleation of a low-temperature phase and subsequent stress-induced growth of the secondary phase (stress-induced phase separation). With further temperature decrease, an insulator-metal transition takes place at 157 K (= $T_{IM}$).
The bottom panel of Fig. 3 shows integrated intensities of the magnetic Bragg reflections. The three magnetic reflections, that is, F-, A- and CE-types, seem to appear at the same temperature near $T_{IM}$. The F- and A-type (CE-type) components can be ascribed to the long-c (short-c) phase based on the lattice constants. The magnetic ordering at lower temperatures below $T_{CO}$ contradicts to the percolation model. In addition, the volume ratio of the insulating short-c component rather decreases with cooling.

A new scenario for the insulator-metal behavior
is as follows. With a decrease in temperature below $T_{CO}$, the system is transformed from a single phase (Fig. 4(a)) to the two-phase state (Fig. 4(b)), possibly due to the stress-induced phase separation. These phases, that is, the short-c and long-c phases, can be ascribed to the COI and paramagnetic insulating (PI) phases, respectively. With further decrease of temperature below $T_{IN}$, the long-c phase indicates a PI to FM phase transition (Fig. 4(c)). If the metallic region were connected, the apparent insulator-metal transition would be observed.

Yutaka Moritomo and Akihiko Machida
Nagoya University
E-mail: moritomo@cirse.nagoya-u.ac.jp

References