Phase Diagram and Magneto-Transport Properties in $Nd_{1-x}Sr_xMnO_3$ Crystals

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Abstract

We have investigated electronic transport and magnetic properties of $Nd_{1-x}Sr_xMnO_3$ crystals with controlled band filling ($0.5 \leq x \leq 0.8$) grown by the floating zone method. The detailed phase diagram of over-doped $Nd_{1-x}Sr_xMnO_3$ was obtained through magnetization, resistivity, and crystal structure measurements. We have found the phase boundary from an insulator with tetragonal symmetry to a metal with pseudocubic one at high temperatures $\approx$ 450 K. The observed insulator-metal phase transition is attributed to the orbital order-disorder transition.

Key words: phase diagram; orbital-ordering; metal-insulator transition; manganite

Recently, electron-orbital related phenomena such as orbital order-disorder transitions and orbital waves (or orbitons) attract much interest in the $3d$ transition metal oxides [1]. For example, major origin of colossal magnetoresistance in manganites is the magnetic-field-induced destruction of the charge/orbital ordered state. Almost two-dimensional (2D) charge dynamics in the over-doped manganite are caused by the ordering of anisotropic-shaped $d(x^2-y^2)$ orbital [2]. Experimental evidence for orbiton, which corresponds to the collective excitation of orbital, is lately reported in orbital-ordered states of $LaMnO_3$ by using Raman scattering [3]. Thus, the orbital degree of freedom is thought to be an underlying key parameter for the physics of the $3d$ transition metal oxides including the manganites. We have previously reported a systematic transformation of various orbital-ordered and -disordered states, accompanying the respective spin-ordering features, in $Nd_{1-x}Sr_xMnO_3$ studied by neutron diffraction measurements [4]. The system investigated here, colossal magnetoresistive $Nd_{1-x}Sr_xMnO_3$, shows up complex phase diagram by changing the carrier kinetic energy with doping level x (see also Fig. 2). In the case of x=0.55, the 2D charge-transport due to $d(x^2-y^2)$ orbital ordering subsists even above Néel temperature (T_N), above which anisotropic crystal structure is also expected to still remain. Therefore, we have investigated the charge-transport reflecting the orbital state in a wide temperature range. In this paper we report on the temperature-induced melting transition of orbital ordering and propose a revised phase diagram of over-doped $Nd_{1-x}Sr_xMnO_3$ crystals.

$Nd_{1-x}Sr_xMnO_3$ crystals were grown by the floating zone method. The grown crystals were characterized by powder X-ray diffraction measurements. We have confirmed that the grown crystals were single phase without any secondary or impurity phase except for the sample showing a phase separation in low temperature near the phase boundary ($x\sim$0.63). Measurement of $\rho - T$ curves was performed for the sample heated in a muffle furnace up to 1000 K far above T_N by using standard four-probe method. We have used a calibrated Pt-Pt+13%Rh thermocouple for monitoring temperature. We have not been able to measure the anisotropic transport properties because of a multidomain structure that is not thoroughly eliminated in the present crystal.

We show in Fig. 1 temperature dependence of resis-

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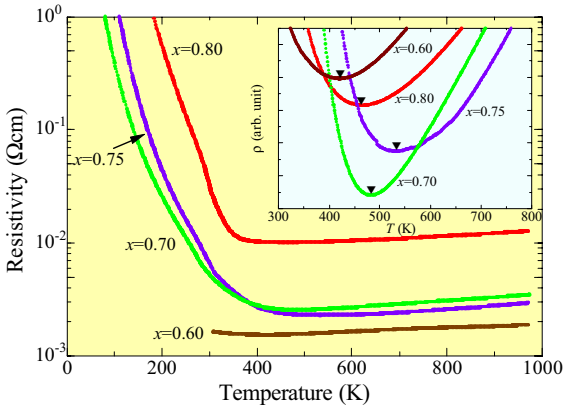

Fig. 1. Temperature dependence of resistivity for $Nd_{1-x}Sr_xMnO_3$ crystals (x=0.6, 0.7, 0.75, and 0.8) in zero magnetic field. The inset shows the magnification of the main panel. The phase transition temperature is indicated by an inverted triangle.

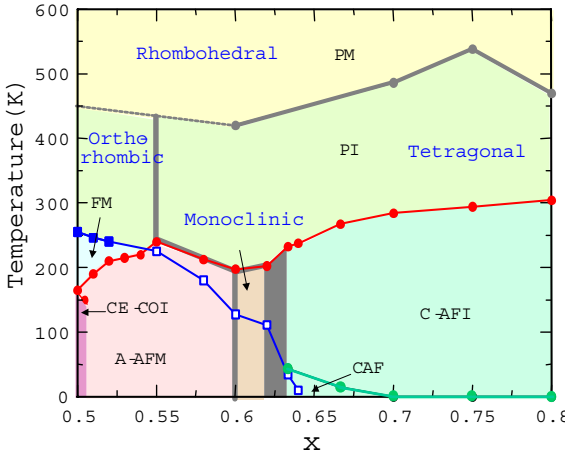

Fig. 2. Electronic, magnetic, and crystallographic phase diagram of $Nd_{1-x}Sr_xMnO_3$ crystal ($0.5 \leq x \leq 0.8$). The abbreviations mean paramagnetic metal (PM), paramagnetic insulator (PI), ferromagnetic metal (FM), CE-type charge-ordered insulator (CE-COI), A-type antiferromagnetic metal (A-AFM), canted antiferromagnetic insulator (CAF), and C-type antiferromagnetic insulator (C-AFI). Open squares mean a paramagnetic Curie temperature. Thick lines are the crystallographic phase boundaries.

tivity for $Nd_{1-x}Sr_xMnO_3$ crystals. In the over-doped manganites with $0.63 \leq x \leq 0.8$, in which the chain-type (C-type) antiferromagnetic (AF) insulator is stabilized below T_N ($\approx$ 300 K), resistivity sharply decreases with increasing temperature, and then shows the minimum point ($\approx$ 450 K, depicted in the inset) and gradually rises up. A slight change in activation energy of resistivity has also been detected at T_N. This insulator-metal phase transition is due to the melting transition of orbital ordering. According to the neutron diffraction measurements [5], lattice structural changes occur at respective temperatures corresponding to the insulator-metal transitions: the tetragonal symmetry ($I4/mcm$) in low temperature phase is changed to the pseudocubic symmetry ($R\overline{3}C$) in high temperature one. In other words, c-axis elongated crystal due to the rod-shaped $d(3z^2-r^2)$-type orbital ordering can be transferred to the nearly cubic one due to the spherical orbital, which is the admixture of $d(3z^2-r^2)$ with $d(x^2-y^2)$. It should be noted that the orbital and charge ordering at these high temperature regions is not static long-range order but dynamical short-range order or a precursor. We cannot observe a direct evidence of charge- and orbital- ordered state such as a superlattice structure in these samples.

We have also confirmed a similar large drop in resistivity at the orbital-ordering transition temperature of $\sim$ 780 K in the parent $LaMnO_3$ compound. In the case of $LaMnO_3$, $d(3x^2-r^2)/d(3y^2-r^2)$-type orbital ordering was clearly observed by synchrotron radiations [6]. We have concluded that large change in resistivity for the present sample arises from the melting of the orbital ordering by comparing the case of $LaMnO_3$.

Figure 2 shows thus obtained phase diagram for $Nd_{1-x}Sr_xMnO_3$ together with the data from Ref. [4]. As reported in Ref. [4], the 2D metallic state with layered-type (A-type) AF state appears for $0.51 \leq x \leq 0.62$. Doping above x=0.62 further alters the magnetic structures to the chain-type. We have found the phase separation near this phase boundary (broad line near at x=0.625) between the A-type-AF metal with monoclinic crystal symmetry and the C-type-AF insulator with tetragonal one. As shown in the figure, spin ordering is decoupled from the orbital degree of freedom similar to the case of the parent material $LaMnO_3$. The thick line located around $\sim$450 K means the phase boundary between the orbital-ordered insulator with tetragonal symmetry in low temperature phase and orbital-disordered metal with rhombohedral one in high temperature phase.

In conclusion, we have observed the resistive anomaly far above T_N in over-doped manganites, which resulted from the temperature-induced orbital order-disorder transition coupled with the Jahn-Teller lattice distortion. The orbital degree of freedom is thought to be indispensable for understanding this rich phase diagram presented here.

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