

Transport and magnetic properties of Sr doped $\text{Nd}_{0.55}\text{Ca}_{0.45}\text{MnO}_3$

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Published online: 12 May 2007
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Abstract The effect of Sr doping on the transport and magnetism properties of charge/orbital-ordered $\text{Nd}_{0.55}\text{Ca}_{0.45}\text{MnO}_3$ is investigated. A low temperature phase transition from a charge/orbital ordered insulator to a ferromagnetic metal was founded in the $\text{Nd}_{0.55}(\text{Ca}_{1-x}\text{Sr}_x)_{0.45}\text{MnO}_3$ samples. The ground state is the charge/orbital ordered insulator at $x < 0.2$, while for $x > 0.3$ it changes to a ferromagnetic metal. The resistivities of the samples exhibit almost ideal percolation behavior with a percolation threshold of 0.3. Therefore, this system shows an intricate competition between metallic ferromagnetism and charge/orbital ordered insulator and the percolation behavior demonstrates that the relative volumes of ferromagnetic phase and charge/orbital phases changes with the doping content x and temperature.

Keywords Colossal magnetoresistance effect · Phase separation · Percolation behavior

PACS number 75.47.Lx · 75.47.Gk · 71.30.+h

1 Introduction

The doped manganites, $\text{RE}_{1-x}\text{AE}_x\text{MnO}_3$, where RE is a trivalent rare-earth cation and AE is a divalent alkaline

cation, have attracted a great amount of efforts because of their great deal of fascinating properties arising from the strong interplay between spin, charge, orbital and lattice degrees of freedom,[1, 2] such as colossal magnetoresistance effects (CMR)[3] and charge/orbital ordered states (CO-OO),[4] and also because of their potential technological applications. The mechanism of CMR effect in manganites is one of the central issues in the physics of strongly correlated electronic systems. The change of resistivity for some manganites can be as big as 10^4 – 10^6 upon an external magnetic field of a few Tesla. The CMR effect can be understood in the framework of the double exchange interaction model (DE).[5] When the rare earth site (A-site) is doped with a divalent ion (AE), a proportional number of Mn^{3+} ions is converted into Mn^{4+} ions and mobile e_g electrons are introduced, mediating the ferromagnetic interaction between Mn^{3+} and Mn^{4+} according to the DE interaction. In these systems, the hopping of e_g electrons between two partially filled d -orbitals of neighboring Mn^{3+} and Mn^{4+} ions via the orbital overlap $e_g - O2p_\sigma - e_g$, and the strong Hund coupling between the t_{2g} core spins and the mobile e_g electrons' spins cause the ferromagnetic interaction between Mn^{3+} and Mn^{4+} .

However, it's now well accepted that the electronic phase diagram of CMR manganites is very complex and the DE model alone is not sufficient to explain the CMR effect and related magneto-transport properties.[6–8] One of the properties of manganites which can't be explained by DE interaction is the charge/orbital-ordered (CO-OO) state, in which the Mn^{3+} and Mn^{4+} ions were arranged regularly and periodically in real space.[1, 4] The recent works allow us to conclude that the CMR effect is a collective phenomenon due to the many-body correlations and different from single particle picture such as transitions from small to large polarons. The competition between some ordering inter-

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actions, such as those between DE ferromagnetic interaction and charge/orbital ordered antiferromagnetic interaction may be important for CMR effect.[6] In relation to the competition between the CO-OO state and ferromagnetic metallic state (FMM), a scenario of the electronic phase separation has recently been arisen as a generic feature of CMR systems, and it has been accepted that given a temperature T and field H the electronic and magnetic ground state of manganites can be inhomogeneous due to the coexistence of FMM phase and charge-ordered antiferromagnetic insulating (AFI) phase, originating from the electronic phase separation.[2, 9, 10] As the carrier concentration varies, various ordering states and phase transitions can be observed. The preference of one ordering state rather than others or coexistence of two or more states depends on doping, pressure (external or chemical), T and H . Consequently, the system property can be very different.

$\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.3 < x < 0.5$) is a typical manganite which exhibits a transition from high-temperature paramagnetic insulating (PMI) phase to a low-temperature CO-OO phase at $T_{\text{CO}} \sim 250$ K. $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$, which has a bigger A-site cation radius than $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$, changes from PMI phase to FMM phase at $T_{\text{C}} \sim 230$ K. Upon the substitution of Ca by Sr in $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$, while keeping the hole-doping concentration constant, there maybe introduce the competition between the CO-OO phase and FM phase in the sample and give some insights into the physical mechanism of the CMR effects. In this paper, we report our experimental investigation on the competition between CO-OO and FMM phases in $\text{Nd}_{0.55}(\text{Ca}_{1-x}\text{Sr}_x)_{0.45}\text{MnO}_3$ ($x = 0.0$ to 1.0). Indeed, a melting of the CO-OO state by chemical substitution at the A-sites will be shown.

2 Experimental procedures

Bulk ceramic samples of $\text{Nd}_{0.55}(\text{Ca}_{1-x}\text{Sr}_x)_{0.45}\text{MnO}_3$ were prepared by the conventional solid-state reaction in air. The highly purified Nd_2O_3 , CaCO_3 , SrCO_3 , MnCO_3 were mixed on stoichiometric ratios, ground and then fired at 1250°C for 24 h in air. The resultant powders were re-ground and pellettized under 3,000 psi pressure to a disk of 1 cm in diameter, then the pellets were sintered at 1400°C in air for 12 h. The crystallinity of the samples was examined by X-ray diffraction (XRD) with $\text{Cu K}\alpha$ radiation at room temperature. The magneto-transport measurements were performed using a standard four-probe method down to 15 K. Magnetic measurements were conducted with a Quantum Design superconductive quantum interfere device (SQUID) magnetometer. The magnetization curves were recorded under a 100Oe field in a warm process after a zero field cooling down to 5 K. The

magnetic loops at 5 K for some samples were also recorded from -5T to 5T .

3 Results and discussion

The x-ray diffraction patterns of $\text{Nd}_{0.55}(\text{Ca}_{1-x}\text{Sr}_x)_{0.45}\text{MnO}_3$ samples with $x = 0.0, 0.1, 0.5$ at room temperature are presented in Fig. 1. All the samples are single-phased and the reflections of all samples can be accurately indexed in an orthorhombic space group ($Pnma$). It is concluded that Sr-doping at Ca sites causes no identified lattice effects and the samples remain single-phased in terms of lattice configuration.

The transport behaviors of all samples were carefully measured over a wide temperature range from 15 to 300 K and resistivity ρ as a function of T is showed in Fig. 2. An overall comparison of the data clearly demonstrates the significant effect of Sr-doping on the magneto-transport behaviors. In general, one sees an overall decrease of resistivity with increasing doping level x . For samples with $x = 0.0$, the resistivity increases with decreasing temperature, and exhibits insulating transport behavior over the whole temperature range. Similarly, the transport at $x = 0.1$ as a function of T again shows an insulating behaviors over the whole T -range, but the resistivity is much smaller than that

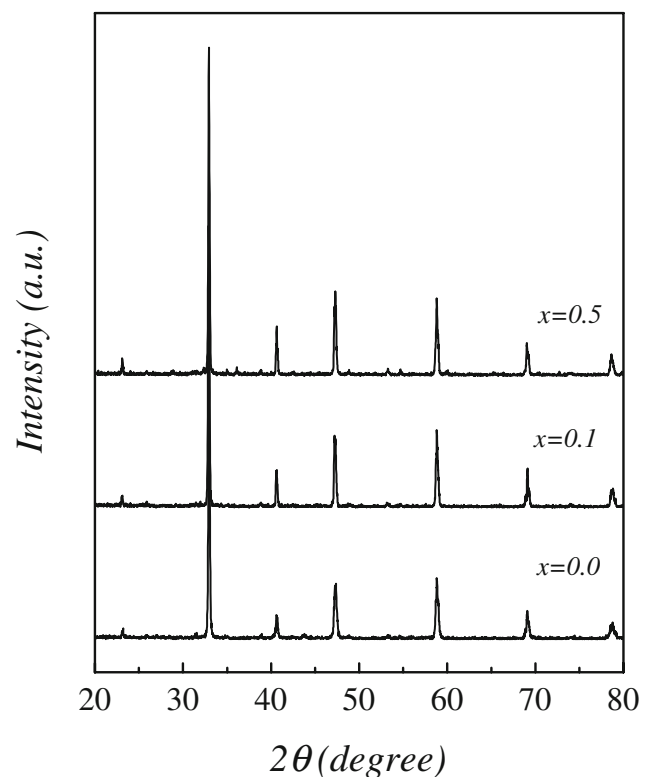


Fig. 1 X-ray diffraction spectra of polycrystalline $\text{Nd}_{0.55}(\text{Ca}_{1-x}\text{Sr}_x)_{0.45}\text{MnO}_3$ samples with $x = 0, 0.1, 0.5$

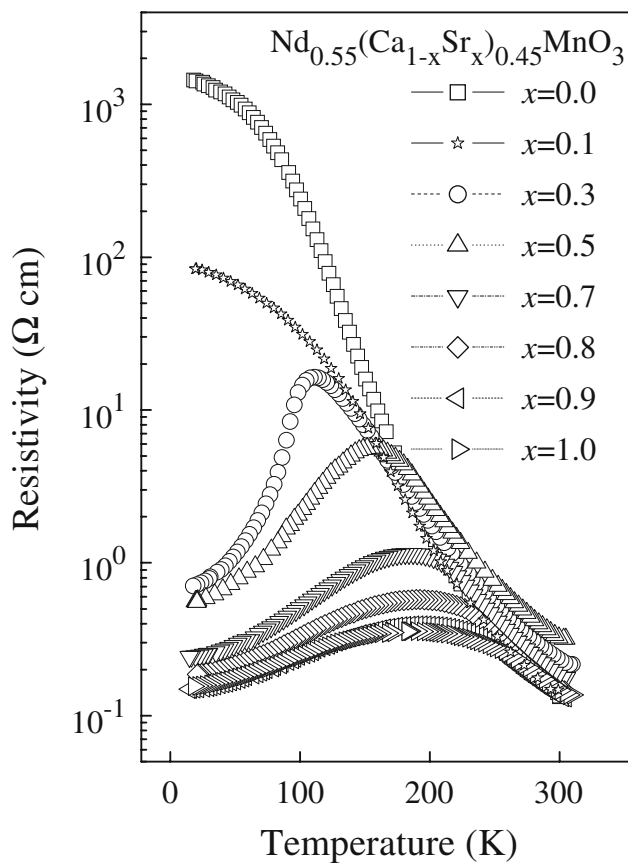


Fig. 2 Resistivity as a function of T under zero-field for $\text{Nd}_{0.55}(\text{Ca}_{1-x}\text{Sr}_x)_{0.45}\text{MnO}_3$ samples from room temperature to 15 K

of the undoped sample ($x=0.0$), especially in the low- T range. With further doping to $x=0.3$, one observes a clear metal-insulator phase transition (MIT) at $T_p \sim 111$ K. Further increasing of the Sr concentration only causes small decreasing of the resistivity, but the MIT point shifts from 111 K at $x=0.3$ to 210 K at purified $\text{Nd}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$ with $x=1.0$, noting that the measured T_p for $x=1.0$ is in agreement with the other's reports.[11]

The magnetic property measurement confirms our above results. The magnetizations as a function of T in a warm process of five samples are showed in Fig. 3. The sample with $x=0.0$ changes to a charge ordered state at $T_{\text{CO}} \sim 250$ K and then to an antiferromagnetic state at $T_N \sim 120$ K which are in agreement with the previous reports.[2] The sample with $x=0.1$ shows a similar magnetic properties to the undoped sample, but the magnetization at low temperature is bigger. The samples with $x \geq 0.3$ exhibit typical paramagnetic-ferromagnetic transition with decreasing temperature, which coincides with the transport properties. And the doping causes the increasing of the magnetization and the Curie temperature. So the magnetic behavior exhibits a transition from charge-ordered antiferromagnetic ground state to a ferromagnetic state and an increasing of the magnetization with Sr doping. According to the transport

and magnetic measurement, we conclude that the Sr doping causes a decreasing of the resistivity and a transition from a charge ordered insulating phase to a ferromagnetic metallic phase.

It is well known that $\text{Nd}_{0.55}\text{Ca}_{0.45}\text{MnO}_3$ is a typical charge ordered antiferromagnetic insulator and $\text{Nd}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$ is a typical ferromagnetic metal at low temperature. The Sr cation with a bigger radius than Ca prefers the FM metallic phase because of the smaller lattice distortion and the DE process.[2] So the distortion of the lattice around Sr ions is suppressed and the DE interaction between the Mn^{3+} and Mn^{4+} becomes possible. In the Sr-doped samples, Sr ions randomly occupy the Ca sites in the lattice, and then the long range charge/orbital order states with antiferromagnetism (AFM) is suppressed and some fragments with short range FM order appear around Sr ions. These fragments are metallic due to the DE interaction and are called ferromagnetic clusters. However, the long range CO-OO phase can not be destroyed completely and the FM metallic phase can not become predominant at low x case. So the long-range CO-OO insulating phase still remains in

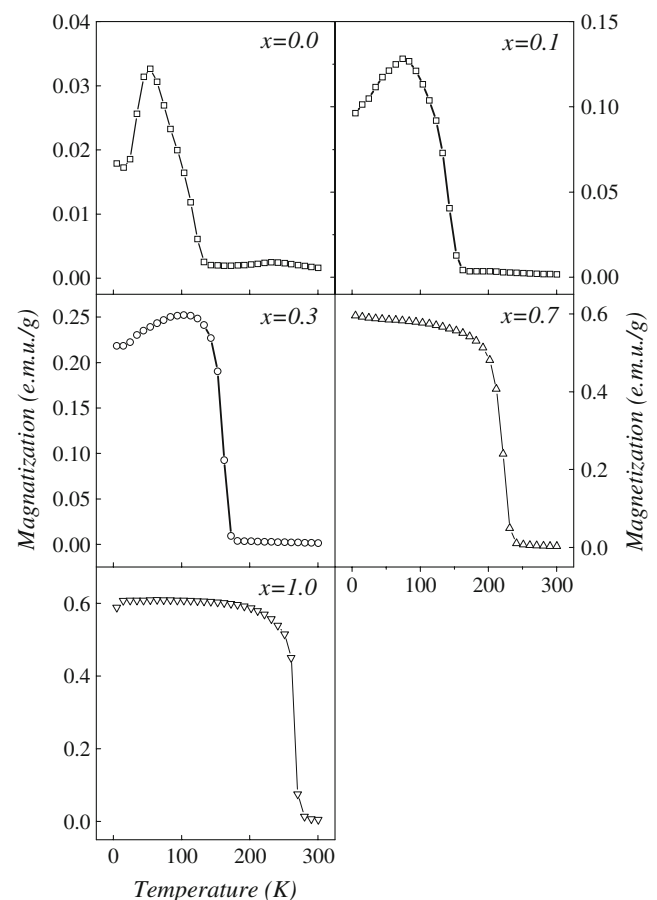


Fig. 3 The magnetization-Temperature curves of five samples with $x=0.0, 0.1, 0.3, 0.7$ and 1.0 in a warm process after zero-field cooling to 5 K

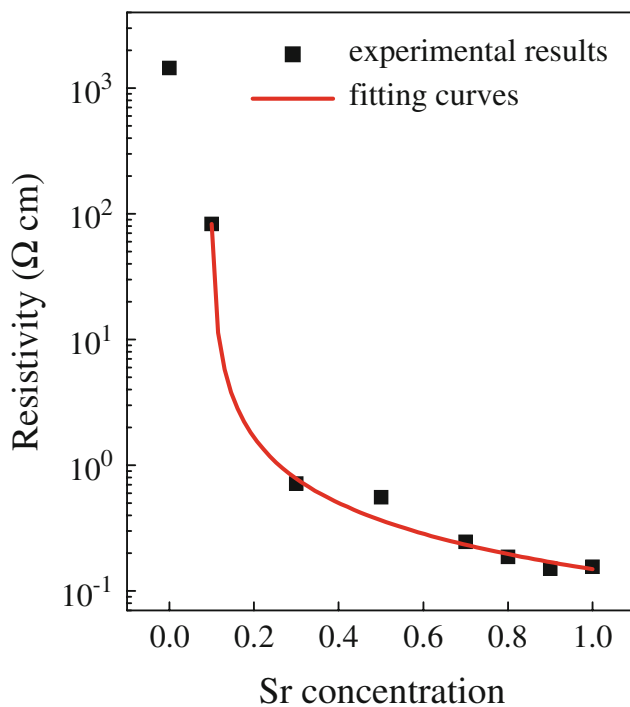


Fig. 4 The resistivity of the samples at 15 K as a function of Sr concentration. The red line is the fitting curves with the percolation conductive law as described in the text

the sample ($x=0.1$) because of the small doping level. The decreased resistivity at low- T range is due to the appearance of the ferromagnetic clusters. Further doping results in the further suppressing of the CO-OO insulating phase as well as the increasing of the size and number of the ferromagnetic clusters, then the further decreasing of the resistivity of the system. When the concentration of Sr is high so that some ferromagnetic clusters around the Sr ions link to each other and a percolation path of conduction comes into being, the ferromagnetic metallic phase becomes predominant and the percolation conductive behavior appears. Then the resistivity of the system decreases significantly and the transport changes to a metallic behavior. This is the reason for the great decrease of resistivities at $x < 0.3$ and the insulator-metal transition of the ground state of the samples at $x=0.3$. The increasing of Sr concentration only leads to the growth of the FM metallic clusters and doesn't cause evident effects on the transports behavior according to the classical percolation picture. Then the resistivities for $x > 0.3$ only decrease slightly accompanying with increasing T_p , but the magnetization increases due to the growth of the ferromagnetic phase. Therefore, the Sr doping at Ca sites in $\text{Nd}_{0.55}\text{Ca}_{0.45}\text{MnO}_3$ causes a percolation of the ferromagnetic metallic clusters and then insulator-metal transition of the ground states.

An evidence of our above statements is that the resistivity at low T follows the percolation behavior. The resistivities of all the samples at 15 K which is the lowest

temperature we can get in are shows against Sr-doping level in Fig. 4. It is obvious that the resistivities exhibit almost ideal percolation behavior in the low temperature. The resistivity of a system with percolation can be described by scaling law $\rho \propto (f - f_c)^{-t}$ where f is the metallic volume ration, f_c is the percolation threshold of the metallic phase, and t is the resistivity exponent.[12] If the volume ratio of the ferromagnetic metallic clusters is represented by doping level x , our results shows a good coincide with the scaling law with $t=2.1$, which is in good agreement with the predicted universal value of $t=2.0$ for 3D percolative conduction [13], as showed by the red line in Fig. 4

Of course, our above explanation is somehow preliminary and qualitative. More direct experimental evidences are required for checking this conceptual picture. The temperature-variable magnetic force microscopy (MFM) may be a good mean to directly observe the appearance, growth and percolation of the ferromagnetic clusters. In fact, the researchers have directly observed these behaviors in Pr doping $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ films by MFM [14]. This is to say the percolation conductive behavior may be popular in manganites. These works are under going on.

4 Conclusion

In conclusion, we have investigated the magneto-transport properties and the behaviors of the magnetic of polycrystalline $\text{Nd}_{0.55}(\text{Ca}_{1-x}\text{Sr}_x)_{0.45}\text{MnO}_3$ samples ($x=0.0\sim 1.0$). The Sr doping causes a great drop of the resistivity and a transition of the ground state from a charge ordered insulating phase to a ferromagnetic metallic phase. Moreover, the resistivities of all samples at 15 K exhibit a typical percolation behavior with a scaling component 2.1 which shows a good agreement with the 3D percolation law. The appearance and percolation of the ferromagnetic metallic clusters are argued to be responsible for the decreasing of the resistivities and the insulator-metal transition of the ground states of our samples.

Acknowledgement The authors acknowledge the financial support of this work from the National Key Project for Basic Researches of China, the National Natural Science Foundation of China through the innovative group project and normal project, and LSSMS of Nanjing University.

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