Orbital ordering changes of Nd$_{1-x}$Sr$_x$MnO$_3$ (x~0.5) under high pressures

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Summary

The synthesized Nd$_{1-x}$Sr$_x$MnO$_3$ (x~0.5) polycrystalline bulk samples show FM, A-type AF and charge ordering CE-type AF transitions on cooling from room temperature to 78K. We consider that the abundant magnetic structures are caused by phase segregation. We have investigated the orbital ordering behavior under hydrostatic pressures up to 7.5 GPa and found that low pressure favors the A-type AF phase with $d(x^2-y^2)$ orbital ordering and the CE-type AF phase with $d(3x^2-r^2)/d(3y^2-r^2)$ orbital ordering, while suppresses the FM phase with disordered orbital ordering; however, high pressure favors the A-type phase and suppresses the CE-type AF phase. Transport property enhancement and large resistance changes under high pressures are observed.

I. Introduction

The colossal magnetoresistance (CMR) effect, simultaneously including a ferromagnetic (FM) and metallic state in the vicinity of the FM transition of manganites, is generally explained by the double-exchange model[1,2]. However, many findings in the transport, magnetic and structural properties have revealed that orbital degree of freedom, Coulomb repulsive interaction, Jahn-Teller effect and superexchange interaction also play very important roles in the CMR effect[3,4]. In doped manganites, the FM metallic state is realized by the coupling of mobile $e_g$ orbital carriers with local $t_{2g}$ orbital spins. As the transfer interaction or the one-electron bandwidth(W) of the $e_g$ carriers decreases, which depends on the Mn-O-Mn bond angle in the perovskites, the FM state will suffer from the competing instabilities such as charge ordering, orbital ordering, or collective Jahn-Teller distortions[3,5]. The one-electron bandwidth can be changed by the mean radius of A site cations, resulting in lattice distortions. There are two types of the charge ordering (CO) transition. One (type I) is the CO state emerging in the FM phase, where the CO instability is not strong[6], and the other (type II) is the CO state occuring at a higher temperature, where the FM phase is no longer present[7]. Nd$_{1-x}$Sr$_x$MnO$_3$ shows complex phase transitions and belongs to type I CO state at x=0.5[6]. For 0.3<x<0.48, the compounds show a FM metallic state as the ground state, and in the region of 0.50<x<0.60, they are in a metallic antiferromagnetic (AF) phase with a layered A-type spin structure[8,9]. With further increase of x, they are in another AF phase with a C-type spin structure[9]. In a very narrow composition range of around x~0.5, on cooling from room temperature, the compound shows a transition from a paramagnetic state to a FM state at about 250K and then a transition from FM state to a CO insulator with CE-type AF spin structure below 160K[8-10]. The crystal structures of the CE-type and A-type AF states are characterized by apically compressed MnO$_6$ octahedra, while that of the C-type AF state is characterized by apically elongated octahedra, reflecting their respective layered-type or rod-type orbital ordering patterns[9]. Moritomo et al.[11] determined the space group of Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ to be $Pbnm$, which is much more common in perovskites, and this symmetry has been assumed in several subsequent papers[8,12-14]. On the other hand, recently, P.M. Woodward et al.[10]. reported that two samples with same composition of Nd$_{1/2}$Sr$_{1/2}$MnO$_3$ prepared by similar manner but using different starting materials show different phase transitions during cooling of the samples. According to the analyses of high-resolution synchrotron x-ray diffraction and neutron diffraction, they found that one of the samples undergoes a phase transition from an orthorhombic phase (FM) with $Imma$ symmetry to another orthorhombic one (A-type AF) with the same symmetry at about 225K, and then a transition from the A-type AF orthorhombic to a monoclinic CO phase (CE-type AF) with $P2_1/m$ symmetry at about 150K. But these three phases can coexist even at a temperature as low as 15K. However, the other sample only shows a transition from orthorhombic FM to CE-type AF monoclinic phase at about 150K without observation of the A-type AF phase.
They explained the different behaviors between the two samples by the slight excess of Mn$^{4+}$ and a wider compositional range for the first sample than for the second one. There are three ground states around $x=0.5$, indicating that the three phases have approximately same energies. Thus, small energy disturbance, for example, caused by temperature, magnetic field\cite{15,16}, strain\cite{17,18} and high pressure\cite{19-21}, etc., can give rise to phase transitions among them.

High pressure, as one of thermodynamic parameters, influences the charge, spin and/or orbital ordering of a sample. Moritomo et al.\cite{19} reported that hydrostatic pressure ($<1$ GPa) increases $T_C$ and decreases $T_{CO}$ in single crystal Nd$_{0.5}$Sr$_{0.5}$MnO$_3$, while Arima et al.\cite{20} reported that uniaxial pressure along the $c$-axis decreases $T_C$ and increases $T_{CO}$ in the same crystal, and stabilizes the A-type AF state with increasing $T_N$ in single crystal Nd$_{0.45}$Sr$_{0.55}$MnO$_3$. Recently, Cui et al.\cite{21} have investigated the transport and structural properties of pressure-induced magnetic states in polycrystalline Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ and found that the $T_{CO}$ increases first with increasing pressure and appears to decrease at pressures above ~3.8 GPa.

In this paper, we report the transport and magnetic properties of the polycrystalline bulk Nd$_{1-x}$Sr$_x$MnO$_3$ ($x \approx 0.5$) at ambient pressure and the transport property under hydrostatic pressures up to 7.5 GPa in order to investigate the orbital ordering behavior under high pressures.

II. Experiments

The polycrystalline bulk Nd$_{1-x}$Sr$_x$MnO$_3$ ($x \approx 0.5$) was prepared using traditional solid state reaction technique. Stoichiometric amounts of Nd$_2$O$_3$, SrCO$_3$, MnO$_2$ and Mn$_2$O$_3$ powders were mixed, ground, pelletized and calcined three times at 1050°C in air for 24 h with intermediate grindings. The pellets thus obtained were reground, pelletized and sintered at 1350°C in air for 48 h, and then cooled down to room temperature in furnace. Transport and magnetic properties of the samples were measured using a Mag Lab System (2000 Oxford UK), and the electrical resistivity of Nd$_{1-x}$Sr$_x$MnO$_3$ ($x \approx 0.5$) under high pressures was measured as a function of temperature by means of the DC four-probe method using the cubic anvil apparatus operated up to 7.5 GPa. The cubic anvil high pressure device was compressed evenly from six directions with six anvil tops, thereby producing a hydrostatic high pressure for a sample sealed in the gasket. Two of the six anvil tops were fixed to metal molds placed at upper and lower sections. The anvil top was made of tungsten carbide, and the gasket material was a mixture of amorphous boron and epoxy resin in 4:1 weight ratio. In the gasket there was a Teflon inner cell used to contain the sample tested. Fluorinert liquid was used as the pressure medium. Low temperatures down to 78 K were attained by a continuous flow of liquid nitrogen.

III. Results and Discussion

The phase structure of the prepared polycrystalline sample Nd$_{1-x}$Sr$_x$MnO$_3$ ($x \approx 0.5$) was checked by x-ray powder diffraction and determined to be an orthorhombic structure with
Imma symmetry. The refined unit cell parameters are $a=0.5432\text{nm}$, $b=0.5470\text{nm}$ and $c=0.7685\text{nm}$, in agreement with the results reported in Ref. [10]. No impurity was detected within the measuring accuracy of the detector.

Temperature dependences of magnetization and resistivity are shown in Figs. 1(a) and 1(b), respectively. Both measurements were performed in the warming course. The R-T curve plotted in Fig. 1(b) can be divided into 5 regions, as marked in the figure. It shows a transition from a paramagnetic (PM) state in region I to FM state in region II at $T_c$ about 258K. In region I, the resistance decreases with increasing temperature, showing a semiconducting behavior, while in region II, on the contrary, the resistance increases with increasing temperature, showing a metallic behavior. This transition is in agreement with that reported by other researchers[6,8,22] though the $T_c$ in this paper is a little higher. With decreasing temperature, there is a FM to A-type AF transition at about 236K ($T_n$), going from region II to region III. Similar transition was also observed in Nd$_{0.45}$Sr$_{0.55}$MnO$_3$ at around 225K[8,10,23] in Nd$_{0.49}$Sr$_{0.51}$MnO$_3$ at about 200K[9] and in Nd$_{0.49}$Sr$_{0.51}$MnO$_3$ below 200K[14]. With further decreasing temperature, a CO CE-type AF state occurs below about 150K and the resistivity increases more steeply in region IV with decreasing temperature. In region V where the temperature below about 91K, the resistivity decreases with decreasing temperature, showing a metallic behavior. As determined by neutron diffraction experiments[8-10,24] the A-type AF has a layered spin structure with $d(x^2-y^2)$ orbital ordering, where the spins couple with each other ferromagnetically in ab plane and anti-ferromagnetically along the c-axis. It is also predicted theoretically that this spin ordering should be accompanied by the $d(x^2-y^2)$ type FM orbital ordering[25,26]. However, the CE-type AF state has an AF spin structure with $d(3x^2-r^2)/d(3y^2-r^2)$ orbital ordering accompanying the CO state. The behavior of our sample is markedly different from that reported for single crystal Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ by Kuwahara et al.[6] and Kawano et al.[8] in which a sharp transition from the FM to the CE-type AF phase was observed at ~160K without observation of the A-type AF phase, but our result is consistent with the phase segregation results reported in Refs.[10,16]. Ritter et al.[16] reported that at $H=0$ and 125K, Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ would segregate into two different crystallographic structures with three magnetic phases: i.e. orthorhombic (Imma) FM (19%), orthorhombic (Imma) A-type AF (21.6%), and monoclinic ($P2_1/m$) CO CE-type AF (59.4%) phases. Woodward et al.[10] reported that very small changes in the $\text{Mn}^{4+}:\text{Mn}^{3+}$ ratio caused by either cation vacancies or oxygen off stoichiometry could stabilize the FM state when $\text{Mn}^{4+}:\text{Mn}^{3+}<1$, and stabilize the A-type AF state when $\text{Mn}^{4+}:\text{Mn}^{3+}>1$ in the CO phase, which would give rise to phase segregation. Due to the ferromagnetic coupling of spin and orbital in ab plane in the A-type AF structure, the transport property is anisotropic. Kuwahara et al.[27] reported on the metallic transport property in ab plane and insulating behavior along the c-axis in the A-type AF Nd$_{0.45}$Sr$_{0.55}$MnO$_3$ crystal. The metallic behavior is also reported in Ref. [23]. But in our experiments, the transport property shows semiconductor behavior in the A-type AF phase, which might be due to the polycrystalline bulk sample used in our case. Such a behavior was also observed by Moritomo et al.[14] in Nd$_{0.46}$Sr$_{0.52}$MnO$_3$ and Kajimoto et al.[9] in Nd$_{0.49}$Sr$_{0.51}$MnO$_3$. Due to the emergence of the FM order that coexists with the CE-type AF spin order, the increase of the resistivity is suppressed below ~91K in region V. Such a behavior was also observed by Kajimoto et al.[9] in Nd$_{0.51}$Sr$_{0.49}$MnO$_3$. The phase segregation in our sample may be caused by either the slightly inhomogeneous composition in the sample or the intrinsic nature due to approximately the same free energies of the three phases. Correspondingly, the temperature dependence of the magnetization (M-T) curve presented in Fig. 1(a) shows different features with the variation of temperature. With decreasing temperature, the magnetization (M) increases at $T_c$ (258K) due to the transition from PM to FM state, and appears a little fluctuant at $T_n$ (236K). At $T_{CO}$ (153K), the M value starts to decrease and then keeps almost the same value below 91K, thus verifying the coexistence of the FM and CO phases at low temperatures. The behavior of the measured M-T curve can be well explained with the viewpoint of phase segregation.
Figure 2 shows the resistance versus temperature under hydrostatic pressures up to 7.5 GPa. Only the CO transition is seen in the data obtained at 1.5 GPa without the appearance of FM state. The CO transition temperature at 1.5 GPa is a little higher than that at ambient pressure. With increasing pressure up to 3.0 GPa, the CO transition temperature also increases while the resistance decreases in the whole temperature range, showing an increased transport property under high pressure. With further increasing pressure to and above 4.5 GPa, it is impossible to distinguish the A-type and CE-type AF regions and the resistance is further reduced in the whole temperature range. The temperature dependence of the resistance displays an A-type AF character at and above 4.5 GPa. According to the results shown in Fig. 2, we propose a possible scenario of phase transition under high pressure for the sample studied. As mentioned above, there exist very close correlations among the FM, A-type AF and CE-type AF states. With increasing pressure, at the beginning stage both the CO CE-type AF and A-type AF states are favored simultaneously at lower pressures, while the FM phase is suppressed. But later at higher pressures, the A-type AF phase grows at the expense of the CE-type ordered region. In our experiments, the FM phase is suppressed at below 1.5 GPa, accompanying the vanishing of the metallic transport behavior in the temperature range of 236–258K as well as below 91K. In the normal case, high pressure increases the one-electron bandwidth and enhances the itineracy of \( e_g \) electrons through changing the Mn-O-Mn bond angle and Mn-O bond length, and suppresses the CO state and favors the FM phase[19]. The suppression of CO states under high pressure was also observed in many other perovskites. For example, Moritomo et al.[11] reported that high pressure suppresses the CO state of the Pr\(_{1-x}\)Ca\(_x\)MnO\(_3\) compounds \((x=0.35, 0.4, 0.5)\), which have a narrow one-electron bandwidth, and it also induces a metallic transition from a CO insulator to a FM metallic phase. In contrast to the normal case, there are also some examples in which high pressure increases \( T_{CO} \) and decreases \( T_c \), thus the CO state is favored while the FM state is suppressed. For example, Arima et al.[20] reported that the uniaxial pressure along the c-axis raises the charge and orbital ordering temperature in the Nd\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\) compound. Moritomo et al.[11] reported that with increasing pressure, the resistivity is suppressed and \( T_{CO} \) gradually increases in the compound (Nd\(_{0.5}\)La\(_{0.5}\))Sr\(_{0.5}\)MnO\(_3\) with increased bandwidth and they suggested a transition from the CO CE-type AF to the A-type AF state. The phenomenon of pressure-enhanced \( T_{CO} \) transition was also observed in (Nd\(_{0.5}\)Sm\(_{0.5}\))Sr\(_{0.5}\)MnO\(_3\)[19]. Recently, Cui et al.[21] found that in polycrystalline Nd\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\) the \( T_{CO} \) would increase with pressure below 3.8 GPa but decrease above this pressure. Consistent with the results in Ref. [21], the \( T_{CO} \) also increases with pressure below 3~4.5 GPa in our experiment, but we have not observed the decrease of \( T_{CO} \) at higher pressures due to the suppression of the CE-type AF state. We think there are some differences between the two experiments. For example, their sample only show FM and CO CE-type transitions with decreasing temperature, while ours show FM, A-type AF and CE-type AF transitions. Besides, the \( T_{CO} \) is defined as the transition point of the FM and CE-type AF states in their resistivity curve, while it is defined as the transition point of the CE-type AF and A-type AF phases in our case. Similar to the uniaxial case, in our experiment the hydrostatic pressure may increase the c-axis distortion and decrease the distortion in ab-plane. Since CO state corresponds to a higher orthorhombic distortion state[6] and has a CE-type AF spin structure with \( d(3x^2\cdot r^2)/d(3y^2\cdot r^2) \) orbital ordering, it is favored under high pressures due to the shrinkage of the c-axis, whereas the FM state with disordered orbital ordering is suppressed. The shrinkage of the c-axis also favors the A-type AF state due to its \( d(x^2-y^2) \) orbital ordering. The
increase of the c-axis distortion and decrease of the distortion in ab-plane in Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ with variation of pressure have also been observed by Cui et al.[21] through structural measurements. Kawano et al.[6] reported that the c parameter of the orthorhombic cell shrinks about 1% at the CO transition temperature accompanied by the cooperative Jahn-Teller distortion in Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ and 2.7% at the A-type AF transition $T_N \approx 230$K in Nd$_{0.45}$Sr$_{0.55}$MnO$_3$. Woodward [10] analyzed the cell volumes at 100K and below, and found that the cell volume is systematically larger than the weighted average volume, which is essentially the same as that of CE-type AF phase, while the cell volume of the A-type AF phase is significantly smaller than the average volume. So it is reasonable that high pressure prefers the CE-type AF and A-type AF states to the FM state at the initial stage, and finally favors the A-type AF and suppresses the CE-type AF state. Also high pressure can widen the one-electron bandwidth, and this is also a possible factor to favor the A-type AF phase with $d(x^2-y^2)$ orbital ordering under high pressure at the final stage[8]. In both the CE-type and A-type states, resistivity is reduced due to the enhanced $ab$-plane transfer integral by the reduction of $ab$-plane distortion[21], so the decrease of resistance under high pressure is always observed in the whole measuring range of temperature.

According to the derivative analyses of curves in Fig. 2, the $T_{CO}$ at different pressures are determined and shown in Fig. 3.

Generally magnetic field reduces the resistance of many doped perovskite manganites due to the enhanced double exchange interaction, and magnetoresistance (MR) can be defined as $MR=(\rho(T,0)-\rho(T,H))/\rho(T,0)$, where $H$ denotes the external field and $\rho(T,0)$ and $\rho(T,H)$ represent the resistivities at zero and H fields, respectively. Due to the change of charge, spin and orbital ordering under high pressures, the transport property will also be changed with pressure. In a similar way, we also can define the pressure-induced resistance change (PR) as $PR=(\rho(T,0)-\rho(T,P))/\rho(T,0)$, where $P$ denotes the external pressure and $\rho(T,0)$ and $\rho(T,P)$ represent the resistivities at ambient and P pressures, respectively. Since the measurements at ambient pressure and high pressures in our experiment are carried out using two pieces of the same sample, we replace $\rho(T,0)$ with $\rho(T,1.5\text{GPa})$ to calculate PR in this paper. Large PR values (30~90%) are observed in the whole temperature range at different pressures and the PR increases with pressure at a constant temperature. It can be imagined that the PR value will be increased much more if it is calculated by using $\rho(T,0)$.

\section{Conclusions}

The Nd$_{1-x}$Sr$_x$MnO$_3$ ($\sim x=0.5$) synthesized by solid-state reaction shows FM, A-type AF a CE-type AF transitions with decreasing temperature. Such complex phase transitions are considered to be caused by phase segregation owing to the possible cation vacancies and/or oxygen content off stoichiometry. At the beginning stage, at lower pressure, high pressure favors the A-type AF phase with $d(x^2-y^2)$ orbital ordering and the CO CE-type AF phase with $d(3x^2-r^2)/d(3y^2-r^2)$ orbital ordering, while it suppresses the FM phase with disordered orbital ordering. At the much later stage at higher pressures, the A-type AF phase is the dominant one with the suppression of CE-type AF phase. The decrease of resistance in the whole temperature range under high pressures is due to the enhanced itineracy of $e_g$ electrons in $ab$-plane, caused by the increased transfer integral under high pressures. PR is defined in a similar way of MR, and shows large negative values under high pressures.

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