Direct observation of percolation and phase separation in $Pr_{5/8}Ca_{3/8}MnO_3$ system

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Jump-like magnetization has been study in $Pr_{5/8}Ca_{3/8}MnO_3$ system. The results prove that, above T=5K about, the jump breadth in *M-H* curve suggests a typical AFM-FM transition drove by the magnetic field in different parts of the materials. This can be understood in the picture of phase separation with percolation properties. For lower temperature below 5K, the jumps become ultrasharp with a very narrow width of 1×10^{-4}T. These properties can be explained by magnetostriction and the orbital occupancy of the e_g electron of Mn^{3+}, which reflects the importance of interplay among spin, charge and orbital freedom in present manganites.

INTRODUCTION

In perovskite-type manganese oxides, the strong correlations among spin, charge, orbital, and lattice degrees of freedom play important roles. The charge-order (CO) state can be melted by the application of magnetic/electric fields, x-ray and so on [1-3], which meanwhile is accompanied by some Jahn-Teller distorted MnO_6 octahedra. On the other hand, accumulating theoretical and experimental evidence indicates that the important feature of the manganites is phase separation (PS), which shows the coexistence of the submicrometer CO phase and ferromagnetic (FM) metallic phase [4]. Application of the magnetic field can lead to a collapse of the charge-ordering gap and there is accompanied with a structural PS as well as with the magnetic phase transition [5]. However, this COAFM state is particularly robust in the compounds $Pr_{1-x}Ca_xMnO_3$ systems, owing to its small average A-site cationic radius. In general, very high magnetic fields larger than 20T are needed to overcome this state via a metamagnetic transition. Interestingly, several unexpected and intriguing magnetization steps were recently observed for Mn-site substituted manganese oxides [6-7], where the Mn-substituted weakens the COAFM state and favors the development of PS, then make the required magnetic fields decrease. And it has been proposed that this magnetization transition is related to the martensitic character associated with strain between the PS regions [8]. One should pay attention to the COAFM-FM transition at very low temperature to be ultrasharp and even there appears multiple steps as a function of magnetic field. This intrinsic magnetization steps is different from the traditional metamagnetic transitions. But the satisfying microscopic origins of the observed jumps or steps are not clear at this stage. This set of features has prompted us to undertake a systemic study about this peculiar COAFM-FM transition. Compared to the weakened Mn substitution systems, the $Pr_{5/8}Ca_{3/8}MnO_3$ system was chosen in present work. Based on belonging to phase-separated compound, it should be reasonable to predict that the unusual *M(H)* jumps might be observed in $Pr_{5/8}Ca_{3/8}MnO_3$ as the magnetic field and temperature vary.

EXPERIMENTAL DETAILS

The sample with a $Pr_{5/8}Ca_{3/8}MnO_3$ formula was prepared by conventional solid-state reaction in air. The sample crystallization is good enough and shows good single-phase orthorhombic structure by using XRD analysis (Ragaka 18kWD/max-2500 diffractometer, $Cu-K_\alpha$ radiation). Magnetic and electric measurements were carried out using Physical Property Measurement System (PPMS-9, Q/D Inc.) with the precision 20nV for voltage, and 0.02mT for the magnetic field. The resistivity vs temperature *R-T* curves measured under applied DC magnetic fields from 0-6 T were recorded in a temperature range of

1.9-300K with a precision of 0.01K. The experiment can be well repeated.

RESULTS AND DISCUSSION

The temperature dependence of the resistivity is shown in figure 1 under 0-6 T with both cooling and heating process for $Pr_{5/8}Ca_{3/8}MnO_3$ system. Both the resistivity under zero-field and 3 T are insulating, and the curve shows a discernible upturn around 230K, which is corresponding to the CO onset. A superlattice structure has been confirmed below 230K for $Pr_{5/8}Ca_{3/8}MnO_3$ as a further evidence of the $d_{3x^2-r^2}/d_{3y^2-r^2}$ type of charge/orbital ordering by low-temperature transmission electron microscopy [9]. Application of a magnetic field under 6 T drastically modifies such an insulating CO state, the ρ-T curve is metallic and the Curie temperature is $T_C \approx 84K$ (cooling curve). Meanwhile, the transition becomes strongly hysteretic which display the first-order-type transition in the system.

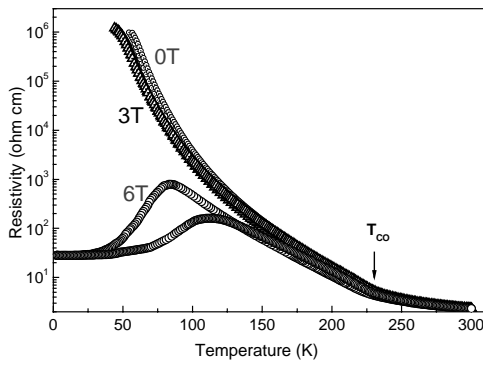Figure 1. The temperature dependence of resistivity under 0T, 3T, and 6T for $Pr_{5/8}Ca_{3/8}MnO_3$. The resistivity was measured in a FC mode.

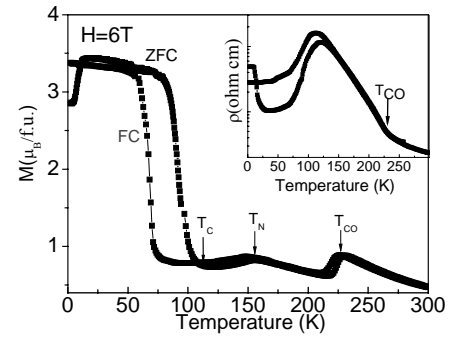Figure 2. DC magnetization M vs temperature in a field of 6T for $Pr_{5/8}Ca_{3/8}MnO_3$ Inset displays resistivity curves recorded in the same conditions.

Figure 2 shows the temperature dependence of the magnetization M measured on heating after the sample was either zero field cooled (ZFC) or field cooled (FC, H=6T). The inset displays resistivity curve recorded in the same conditions. Here, two kinks correspond to the T_{CO} and T_N, around 240 and 160 K, respectively, and at low temperature, an abrupt increasing M is associated with the onset of FM ordering. Below about 100K, ZFC and FC curves separate from each when approaching PS region. This property points to the first order character for FM transition. Another prominent feature is appearance of a steep rise for the ZFC curve with increasing temperature between 4 and 12K. Such behaviors could be connected to the development of the FM phase in the AFM matrix, which shows the temperature dependence of the COAFM/FM coexistent phase. It must be noted that the difference between the values of the M for the ZFC and FC curves around 100K may be related to the large magnetostriction present in this materials. The ρ-T curves recorded in the ZFC and FC modes split at near T<100K, whose behavior is similar to that of magnetization. In the low-temperature region (T<100K), the ρ and M curves vary exactly in opposite ways, which is qualitatively consistent with the simple DE model. This behavior is more difficult to understand for $Pr_{1-x}Ca_xMnO_3$ with a smaller one-electron bandwidth W. According to the DE model, if the localized t_{2g} spins are considered classical and with an angle θ between nearest-neighbor ones, the transfer integral t of e_g electrons between $Mn^{3+}(t_{2g}^3 e_g^1)$ and $Mn^{4+}(t_{2g}^3 e_g^0)$ ions can be expressed as $t = t_O \cos(\theta/2)$, where the t_O is the transfer integral in a fully spin-polarized state. The value of the t is typically 0.2eV in narrow band manganese oxides such as PCMO [10]. Then the electron-phonon coupling constant λ can be evaluated according to $\lambda = \sqrt{2E_{JT}/t}$, where the static JT energy E_{JT} is estimated as 0.25eV at low temperature. Though the E_{JT} is temperature dependent, in present paper we can conjectured that the application of the H align the Mn t_{2g} spins via the Zeeman coupling, which leads
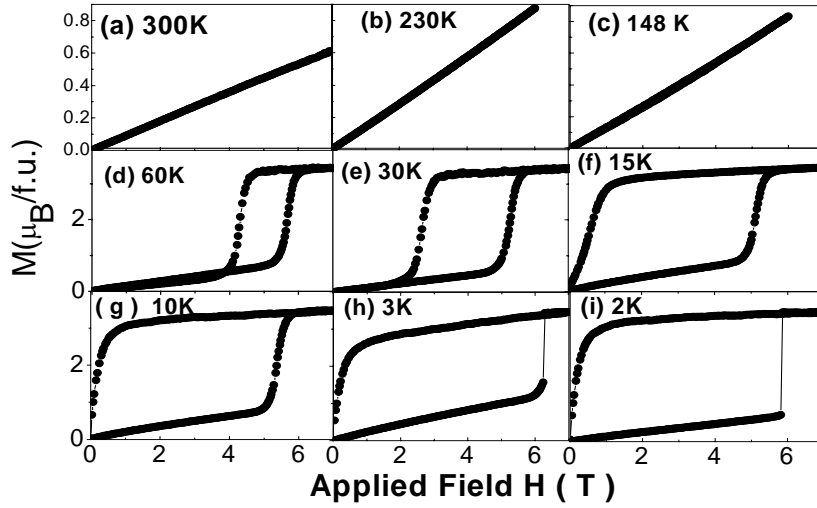
Figure 3. *M(H)* curve at various temperatures under a $0 \rightarrow 7T \rightarrow 0$ circular sweeping model for $Pr_{5/8}Ca_{3/8}MnO_3$. For each run, the sample was cooled in zero field and after stabilization, the measurement was done.

to a decrease in θ and an increase in t, and then induces the behavior of ρ and M for $Pr_{5/8}Ca_{3/8}MnO_3$ to become more in line with the DE model. Actually, applied field H in the COAFM state can melt the CO and cause the change of the electronic and lattice structure, and then favor the stabilization of FM phase.

The magnetization isotherms at various temperatures are given in figure 3. It can be seen that the M is strongly dependent on the thermal and magnetic history. The data at 300K, 230K and 148K are all increase nearly linearly in lower field than 6T. However, for the same magnetic field, the values of the M increase as the temperature decreases. Which probably displays the alternation of the magnetic phase as the temperature reduces. The two-phase nature at the low temperature (<60K) region becomes more evident. In the other hand, an initial AFM state increases with H, which probably is resulted from a reduced canting angle due to canted AFM state or of the field-induced melting of CO [1]. At a sufficiently high H, a field-induced kink occurs associating with the conversion of COAFM to FM. The similarity has been observed in other manganites such as $Pr_{0.5}Ca_{0.5}Mn_{0.95}O_3$ and $La_{0.250}Pr_{0.375}Ca_{0.375}MnO_3$ [7]. And a saturate magnetization appears with a saturation moment of 3.45 μ_B/formula unit at 7T, which is consistent with the result excepted for $Pr_{5/8}Ca_{3/8}MnO_3$ and we can regard this highly magnetization as a fully spin-polarization. When the field is reduced from 7T, the *M(H)* for temperature above ~30K remains in the FM state initially and then appears a AFM-FM transition. However, below ~10K, the *M(H)* behaviors similar to a long range ferromagnet only with a rapid decrease H to 0. At 15K, the *M(H)* seem to show the transition process due to its a sign of AFM as magnetic field is down to 1T. As in figure 3, the breadth of the field-induced kink from AFM-FM suggests the process that magnetic field drive this transition in different parts of the sample. This is consistent with the PS picture with percolation properties. This transition may be explained according to the martensitic effects associated with strain between the PS regions [8]. This behavior changes dramatically at below ~3K, which shows an abrupt step near H_c=6.3T and 5.8T for T=3K and 2K, respectively. Whose width are smaller than 1×10^{-4}T and there wasn't seems to display the percolation process for this transition as it did when temperature above ~3K. After the step, *M(H)* increases nearly linearly with a relatively small slop until it reaches to the FM saturation moment. In fact, the COAFM-FM transition is due to the melting of CO in the system because of the application of magnetic field. The CO is accompanied by an ordering of e_g orbital of the $d_{3x^2-r^2}/d_{3y^2-r^2}$ type and the cooperative Jahn-Teller distortion, then the field-induced alter of the superstructure and magnetic structure may determine the change of the magnetization. The charge and /or orbital occupied scenario and the unique magnetic structure have been determined by neutron diffraction [9]. Just contrary to the "x=1/2 plus defects" scenario due to x away from 0.5, there are without defects to be constructed into the specific charge arrangements. For $Pr_{5/8}Ca_{3/8}MnO_3$, the ratio of Mn^{3+} and Mn^{4+} in the sublattice is 5:3 according to the chemical composition, except that the alternation of $(3x^2-r^2)$ and $(3y^2-r^2)$ orbitals appears in the a-b planes, the extra e_g electrons occupy $3d_{3z^2-r^2}$ orbitals on the Mn^{4+} sublattice which is along the c direction instead of parallel to the ab layers [11]. It is noted that the

Coulomb interaction in this charge lattice state is lowest and play an important role to the experimentally observed CO phase. The magnetic structure at low temperature is commonly refereed to as the pseudo-CE type for the $Pr_{5/8}Ca_{3/8}MnO_3$ [10]. Based on above results, we can conjecture a scenario in which steps may occur. Under normal circumstances, the FM coupling along the c axis would behave like a 1D conductor, because electrons can hop freely in terms of DE mechanism. However, in the a-b plane electron hoping along the FM zigzag chains is arrested by the Coulomb repulsion from the neighboring electrons out of the chain. This is why the solid is an insulator at even very low temperature. If the magnetic field is applied, the ab plane may expand while the c axis is compressed which will improve the orbital overlap within the plane and enhance the probability of the charge transfer. This phenomena will means the possible presence of $d_{x^2-y^2}$ orbital ordering and thus increase the transfer integral t of the e_g electrons and increase the FM interaction. The character of the preferred e_g states under magnetic field are similar to that of $La_{1-x}Sr_xMnO_3$ [12]. Furthermore, when the applied magnetic field is enough large, the ab plane will behave a FM characteristic and make the system a truly 3D conductor. Just in this critical magnetic field, the CO melts completely and the magnetization jumps occur. According to Tokunaga et al. argued [5], the destruction of the orbital ordering by an external field gives rise to the structural phase transition and the recovering of the DE, which promotes the polarization of the t_{2g} spins. In the present case, the field-induced magnetostriction occurs which indicates orbital occupancy of the e_g electron of the Mn^{3+} change as the magnetic filed, and then caused the occurrence of the *M(H)* jumps. In a word, the central conclusion raised by our data is that all the Magnetic-field jumps/steps should be related to magnetostriction, indicating the presence of a field-induced change in the orbital occupancy of the e_g electron of the Mn^{3+}, which show the possible appearance of $d_{x^2-y^2}$ orbital ordering. Meanwhile, the data also reflect the unusual importance of interplay among spin, charge, and orbital degrees of freedom.

ACKNOWLEGMENTS

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