Transport and magnetic properties in the ferromagnetic regime of $La_{1-x}Ca_xMnO_3$

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The transport and magnetic properties of single crystals of $La_{1-x}Ca_xMnO_3$ ($x=0.2$, 0.3) have been investigated. The transport and magnetization results of the ferromagnetic insulator, $La_{0.8}Ca_{0.2}MnO_3$, are quite different from those of $La_{0.7}Ca_{0.3}MnO_3$ that falls into a ferromagnetic metal. We have found that the paramagnetic to ferromagnetic transitions observed in $La_{0.8}Ca_{0.2}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ are second and first order using the Banerjee criterion, respectively. The observation of magnetic frustration and Heisenberg exponents derived by the modified Arrott plot favors the existence of short-range charge/orbital ordering in $La_{0.8}Ca_{0.2}MnO_3$ and even in $La_{0.7}Ca_{0.3}MnO_3$.

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Perovskite-type manganites have drawn a great deal of attention over the last few years due to colossal magnetoresistance (CMR) found in this material.[1] Basic mechanism of the CMR phenomenon has been thought to be explained with double exchange (DE) theory.[2] However, recent studies revealed that additional factors such as lattice distortion, orbital ordering, etc., are required to understand the whole picture of the manganite physics. More recently, phase separation scenario that improves the DE theory by employing the charge inhomogeneity concept has been invoked to explain the CMR effect.[3] The charge inhomogeneous phase involves usually the coexistence of metallic ferromagnetic (FM) and insulating charge-ordered antiferromagnetic (AFM) clusters in a microscopic scale. The insulating region primarily attributed to charge ordering phase persists even in far below the Curie temperature (T_C) and competes with the FM phase.[4,5] It is shown that the CE-type short-range or dynamic charge ordering appears at temperatures above T_C.[6] In addition, orbital ordering associated with e_g level in Jahn–Teller distorted Mn^{3+} ion becomes an important factor to affect magnetic ordering and mobility of itinerant electrons.[7]

Recently, we found that $La_{0.8}Ca_{0.2}MnO_3$ single crystal becomes an insulator below T_C,[8] which agrees well with the report by Okuda *et al.*[9] Unlike $Nd_{0.5}Sr_{0.5}MnO_3$[10] or $La_{1-x}Sr_xMnO_3$ [$x=0.12$ (Ref. 11) and 0.125 (Ref. 12)] manganites in which abrupt jumps in resistivity are observed, $La_{0.8}Ca_{0.2}MnO_3$ has a smooth rise in resistivity with decreasing temperature below T_C. On the basis of recent studies of diffuse x-ray scattering[13] and specific heat,[9,14] short-range ordering is likely responsible for the upturn of resistivity below T_C. Along this respect, our efforts have been devoted to scrutinize this intriguing feature in the low temperature regime from a magnetic point of view, which is not well addressed to date. We have thus investigated the dc resistivity and magnetic critical exponents associated with the paramagnetic (PM) to ferromagnetic (FM) transition on the $La_{1-x}Ca_xMnO_3$ ($x=0.2$, 0.3) samples. The modified Arrott method was employed to explore the magnetic behavior in the critical region. In this report, we present the transport and magnetic results on single crystals of $La_{0.8}Ca_{0.2}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ grown by the floating zone technique.

Single crystals of $La_{0.8}Ca_{0.2}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ were obtained by the floating zone method using an infrared radiation convergence-type image furnace that consists of four mirrors and four halogen lamps.[15] The starting ceramic rods were prepared from the solid state reaction of La_2O_3, $CaCO_3$, and $MnCO_3$ with a stoichiometric ratio. Both crystals turn out to be single-phase materials on the basis of the x-ray diffraction data and the electron-probe microanalysis result. The magnetic data were collected using a quantum design MPMS-5 SQUID magnetometer or a PPMS-7 magnetometer. The resistivity measurements were made using a standard four-probe method at a zero magnetic field. Electrical contacts were made with silver paint.

On the basis of the temperature dependence of resistivity for $La_{0.8}Ca_{0.2}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$,[8] metal-insulator (MI) transitions are observed in both samples, occurring at 230 K for $La_{0.7}Ca_{0.3}MnO_3$ and at 176 K for $La_{0.8}Ca_{0.2}MnO_3$. Below the MI transition temperature T_{MI}, $La_{0.7}Ca_{0.3}MnO_3$ exhibits metallic character judged from positive values in $d\rho/dT$. The observed resistivity at 10 K is relatively higher than that of pure metal, implicating the presence of possible short-range localization induced by charge/orbital fluctuations.[7] This is not surprising because recent reports associated with specific heat[9,16] and Hall measurements[14] demonstrate that short-range charge/orbital correlation persists even in the ferromagnetic metallic state. Unlike the transport behavior of $La_{0.7}Ca_{0.3}MnO_3$, a smooth rise in the resistivity curve with a local minimum at 162 K is observed in $La_{0.8}Ca_{0.2}MnO_3$ below T_{MI}.[8] The upturn of resistivity in the low temperature regime is likely associated with short-range ordering. Similar behaviors are also found in the $La_{1-x}Sr_xMnO_3$ ($x=0.12$ and 0.125) samples where charge/orbital ordering correlated with lattice is the likely cause of the upturn in the resistivity curves.[11,12] $La_{0.8}Ca_{0.2}MnO_3$ lies in the vicinity of the critical doping region at which transition from metallic to insulating phase occurs.[9] Therefore, charge/orbital fluctuations would be reinforced in $La_{0.8}Ca_{0.2}MnO_3$ rather than in $La_{0.7}Ca_{0.3}MnO_3$. This is the reason why $La_{0.8}Ca_{0.2}MnO_3$ has higher resistivity and undergoes the resistivity upturn.

Temperature dependent magnetization curves for $La_{0.8}Ca_{0.2}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ are shown in Fig. 1. There is prominent divergence between the FC (field-cooled) and ZFC (zero-field-cooled) magnetization below T_C in both samples. This can be attributed to the magnetic frustration

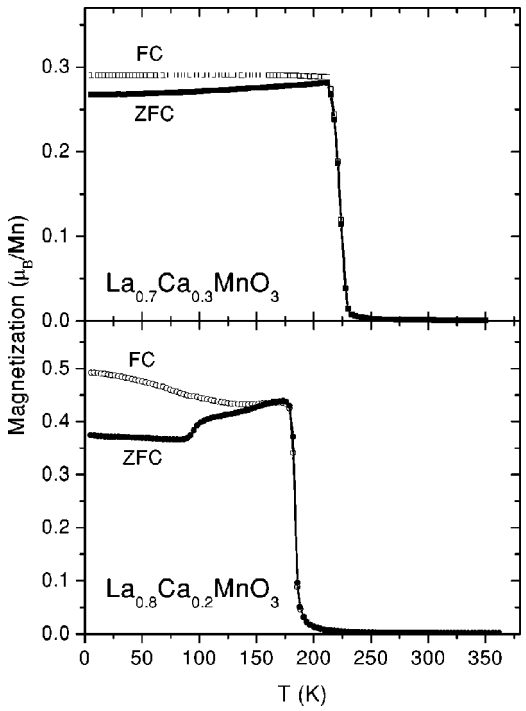

FIG. 1. Top and bottom panels show temperature dependence of magnetization of $La_{0.7}Ca_{0.3}MnO_3$ and $La_{0.8}Ca_{0.2}MnO_3$, respectively.

arising from the competition between FM and AFM interactions, which is evidenced by the frequency dependent ac magnetic susceptibility data.[17] Similar behaviors are also found on single crystals of $Pr_{0.63}Sr_{0.37}MnO_3$ and $Nd_{0.7}Sr_{0.3}MnO_3$.[18] The bottom panel of Fig. 1 clearly shows that $La_{0.8}Ca_{0.2}MnO_3$ is magnetically more frustrated than $La_{0.7}Ca_{0.3}MnO_3$, indicating that charge/orbital fluctuation is enhanced in $La_{0.8}Ca_{0.2}MnO_3$.[9] Small magnetic anomaly near 100 K reminds us of charge-ordered phase transition. For instance, Kuwahara *et al.* carried out the systematic study on a spin-charge-lattice coupled $(Nd,Sm)_{1/2}Sr_{1/2}MnO_3$ system where the antiferromagnetic transition stemming from long-range charge-ordered state coincides with the resistivity steep jump.[19] In $La_{0.8}Ca_{0.2}MnO_3$, the discrepancy between the antiferromagnetic anomaly and the resistivity upturn indicates that short-range charge ordering is likely involved in this system. This conjecture is consistent with the results of the specific heat coefficient relating to the Debye temperature[9] and the orbital fluctuation[7] in the doped manganites.

In order to evaluate the nature of the magnetic transition, magnetization versus magnetic field isotherms of $La_{0.8}Ca_{0.2}MnO_3$ were measured in the vicinity of T_C. As can be seen in the top panel of Fig. 2, the isotherm results show monotonic decrease of magnetization with increasing temperature. The middle panel of Fig. 2 represents the H/M vs M^2 curves where a positive slope is clearly seen in all the M^2 range. According to the Banerjee criterion, the positive slope means that the ferromagnetic to paramagnetic (FM–PM) phase transition is second order.[20] In contrast to this, the bottom panel of Fig. 2 reveals that negative slopes in the

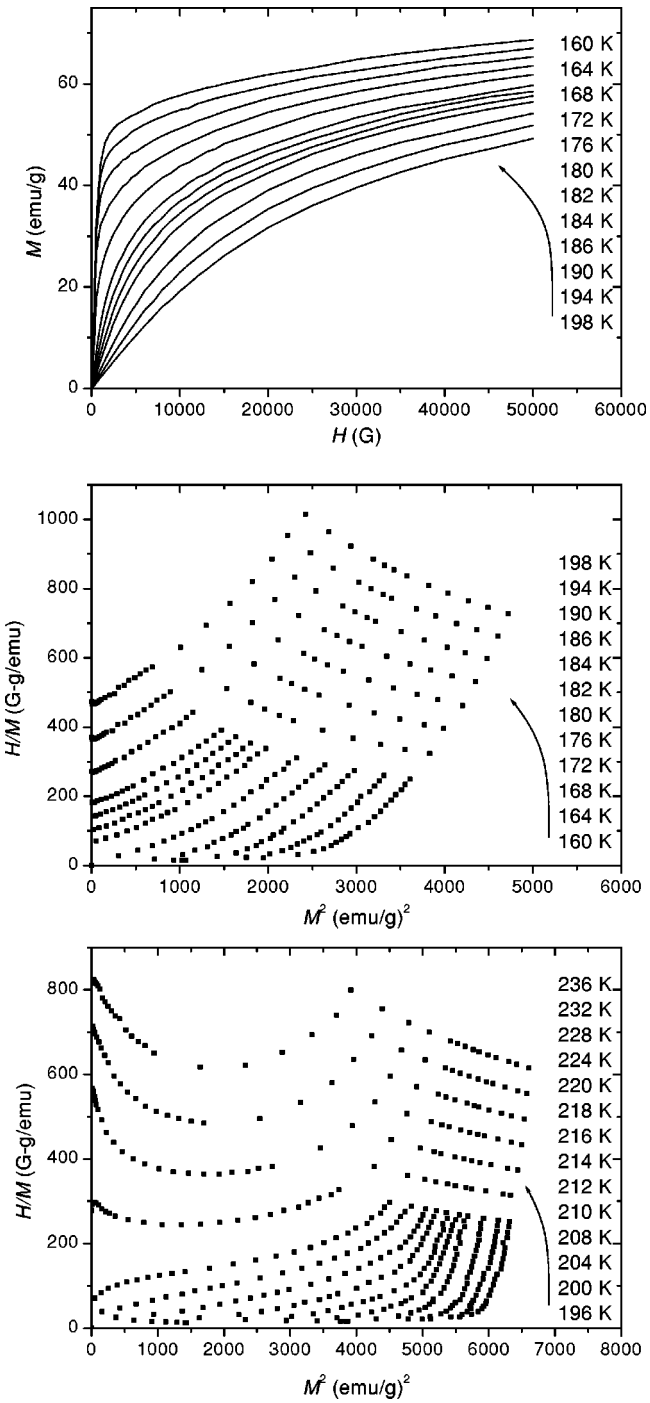

FIG. 2. Top panel exhibits the field dependence of magnetization at temperatures around T_C of $La_{0.8}Ca_{0.2}MnO_3$. Middle and bottom panels show H/M vs M^2 plots for the isotherms of $La_{0.8}Ca_{0.2}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$, respectively. The numbers denote the temperatures of the isotherms.

temperature range 224–236 K are present in the lower M^2 region, signifying that $La_{0.7}Ca_{0.3}MnO_3$ belongs to first order transition. This is consistent with the result found in the polycrystalline $La_{2/3}Ca_{1/3}MnO_3$.[21] This consequence indicates that the character of the magnetic transition is very sensitive to the Ca doping level. The enhancement of charge/orbital fluctuation in conjunction with Jahn–Teller distortion

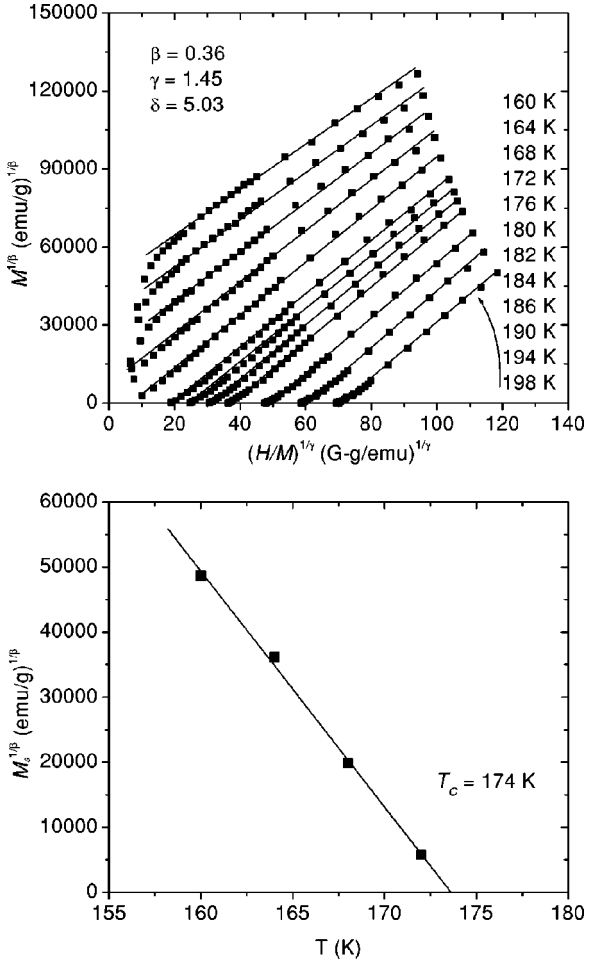

FIG. 3. Modified Arrott plots of magnetic isotherms for $La_{0.8}Ca_{0.2}MnO_3$ are displayed in the top panel. Solid lines stand for best fits. The numbers represent the temperatures of the isotherms. Bottom panel illustrates the temperature dependence of saturation magnetization derived by the modified Arrott plot.

in $La_{0.8}Ca_{0.2}MnO_3$ might be the probable cause of the slope change.[9,14]

In order to assess T_C and a set of critical exponents, β, γ, and δ of $La_{0.8}Ca_{0.2}MnO_3$ in more detail, we employ the modified Arrott plot, $M^{1/\beta}$ versus $(H/M)^{1/\gamma}$, where β stands for the spontaneous magnetization below T_C, γ for the inverse initial susceptibility above T_C, and δ for the critical magnetization isotherm at T_C.[22] In the simple mean field case, the magnetic isotherms should be linear and at T_C the isotherm intersects the origin. As shown in Fig. 3, however, some deviations from the linearity are clearly seen in the isotherm data. An attempt to improve the linearity was made by varying parameters, β and γ, with the modified Arrott method. The isotherm lines are almost straight with parameters of $\beta=0.36$ and $\gamma=1.45$. The value of δ calculated from the Widom scaling relation is 5.03. The saturated magnetization (M_S) is obtained by extrapolating the linear parts of the high field region. From the relation of M_S and T_C in the modified Arrott plot, T_C is given as 174 K, which is shown in the bottom panel of Fig. 3.

The critical exponent values of $La_{0.8}Ca_{0.2}MnO_3$ obtained from the modified Arrott method are close to those expected from the Heisenberg model rather than the mean field theory ($\beta=0.5$ and $\gamma=1$).[23,24] Similar Heisenberg-type behavior has been observed in the perovskite type cobalt oxides, $La_{1-x}Sr_xCoO_3$ $(0.20\leqslant x\leqslant 0.30)$[25] and $La_{0.5}Sr_{0.5}CoO_3$.[26] In the cobalt systems, electronic phase segregation scenario that involves the hole-poor matrix in the hole-rich metallic FM background is introduced to explain the critical exponents. If this scenario deduced from the Heisenberg model applies to the $La_{0.8}Ca_{0.2}MnO_3$ material, one can imagine that there are some ingredients that hinder long-range FM ordering in $La_{0.8}Ca_{0.2}MnO_3$. On the basis of the magnetic and transport data, it is natural to consider that short-range charge/orbital ordering embedded in the FM background is present in this material.

In summary, we have investigated the transport and magnetization of single crystals of $La_{0.8}Ca_{0.2}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$. We have found that the FM–PM transitions of $La_{0.8}Ca_{0.2}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ have second and first order characters using the Banerjee criterion, respectively. Another important finding is that the critical exponents of $La_{0.8}Ca_{0.2}MnO_3$ correspond to those anticipated from the Heisenberg model. From careful examinations of the magnetic data, we have been able to claim that short-range charge/orbital ordering phase persists even below T_C. Hence we believe that the short-range correlation is essential to understand the transport and magnetic properties of $La_{0.8}Ca_{0.2}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$.

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