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Sujoy Roy
Southern Illinois University Carbondale

Naushad Ali
Southern Illinois University Carbondale

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Charge transport and colossal magnetoresistance phenomenon in $La_{1-x}Zr_xMnO_3$

Sujoy Roy and Naushad Ali[a)]
Department of Physics, Southern Illinois University, Carbondale, Illinois 62901-4401

In this study we have investigated the magnetic and electrical transport properties of Zr doped lanthanum manganite perovskite. The structural, magnetic, and transport properties of the Zr doped compounds were determined using x-ray diffraction, dc magnetic susceptibility, and a four probe method for electrical resistivity and magnetoresistance measurements in the temperature range of 5–400 K. The structure of the compounds was found to be rhombohedral. The magnetization versus temperature curves show ferromagnetic regions with the magnetic transition temperatures getting saturated for $x \geqslant 0.07$ compounds. The resistivity curves show decreasing resistivity with increasing Zr content in the compound. The resistivity of the compounds is very high and is explained as due to the localization tendency of the electrons. The metal–insulator transition temperature shows a compositional dependence and has additional contributions apart from magnetism. The results are explained by the double exchange interaction and Mn^{2+}/Mn^{3+} ratio, and also by taking into account the competition between the core-spin interaction and double exchange interaction. [DOI: 10.1063/1.1362653]

INTRODUCTION

The existence of the colossal magnetoresistance (CMR) effect in lanthanum manganites of the form $R_{1-x}A_xMnO_3$ (R=rare earth and A=divalent cation) makes it a candidate for extensive research and technological application. The phenomenon of magnetic phase transition at a particular temperature T_C along with a metal–insulator transition has been traditionally explained by the Zener double exchange interaction.[1] The introduction of a divalent cation in R site results in a Mn^{3+}–O–Mn^{4+} system where three of the four electrons of Mn^{3+} occupy t_{2g} level while the remaining one goes to e_g level. This single electron results in an orbitally degenerate electronic state (^5E_g) and is Jahn–Teller active. On the other hand Mn^{4+} has no e_g electron thereby giving rise to a vacancy (or hole) in the Mn^{3+}–O–Mn^{4+} system. Due to a strong correlation effect the t_{2g} electrons are localized while the e_g electrons can hop depending on the relative configuration of the local spins. However, this simple picture is not enough to explain all the features of CMR and other competitive factors like electron-phonon interaction, polaron formation, charge, and orbital ordering also have to be considered in order to explain the CMR effect.[2–5]

In a hole doped CMR system, the electrical transport is mainly due to hopping of the e_g electron whose magnitude depends on the angle (θ_{ij}) between the neighboring spins.[2] If a tetravalent cation is substituted in the La site of the parent compound $LaMnO_3$ then Mn^{3+}–O–Mn^{2+} system is obtained. In this case there is one electron in the e_g band corresponding to Mn^{3+} but for Mn^{2+} there is no first order crystal field splitting as for d^5 term the net crystal field stabilization is zero. Thus, in such a system the interaction between the e_g electron and the d electron should be large that would cause a change in the CMR effect. The importance of core spin interaction has been studied and reported. Soloviev *et al.*[6] suggests that the t_{2g} process gives rise to antiferromagnetism that can overcome ferromagnetism but due to orbital ordering its magnitude is different along different axes while Millis[7] argues that the strong core spin interaction giving rise to antiferromagnetic interaction may be explained in terms of e_g process only. Golosov *et al.*[8] report that if the double exchange is comparable to antiferromagnetism due to the core spin interaction then the system exhibits ferro or antoferromagnetic order with incomplete saturation.

EXPERIMENTAL PROCEDURE

Ceramic polycrystalline samples of $La_{1-x}Zr_xMnO_3$ ($x = 0.05, 0.07, 0.10, 0.15, 0.20$) were prepared using the conventional solid-state reaction method. Stoichiometric amounts of La_2O_3, ZrO_2, and Mn_2O_3 powder were thoroughly mixed and then heated to 1200 °C for 16 h in air. The samples were then reground, pressed into pellets, and sintered in air at 1280 °C for 10 h. X-ray diffraction (XRD) of the samples was carried out at room temperature in a Rigaku diffractometer in the 2θ ranges of 20°–85°. The magnetization measurements were carried out with a Quantum Design superconducting quantum interference device (SQUID) magnetometer in the temperature range of 5–400 K. The electrical resistivity and the magnetoresistance were measured using the standard four-probe method.

RESULTS AND DISCUSSION

X-ray powder diffraction (XRD) at room temperature showed the formation of single phase compounds with small amount of impurity phase due to Mn_2O_3. The XRD pattern of the compounds can be indexed by a rhombohedral lattice in the space group $R-3c$. The structural parameters were refined by the Rietveld technique.[9] Figure 1 shows the ex-

[a)]Author to whom correspondence should be addressed; electronic mail: nali@physics.siu.edu

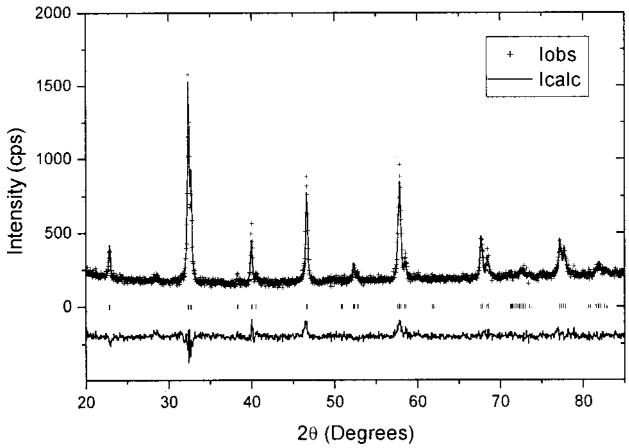

FIG. 1. X-ray diffraction pattern of the compound $La_{0.90}Zr_{0.10}MnO_3$. The experimental data points are indicated by crosses, and the calculated profile by solid trace. The lowest curve shows the difference between the experimental and the calculated data points. The vertical bars indicate the expected reflection positions for rhombohedral structure.

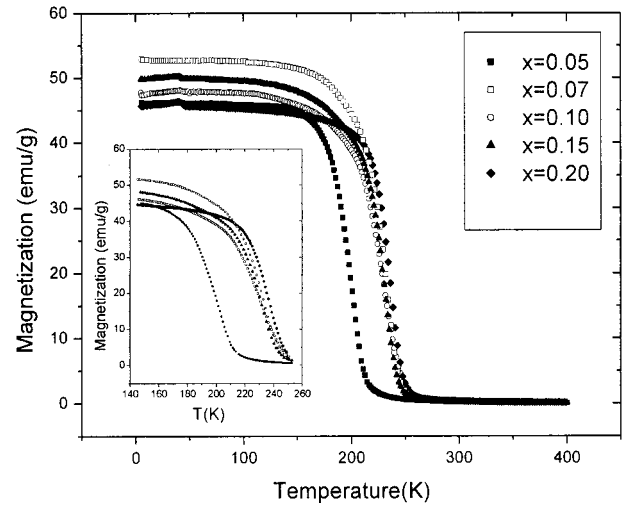

FIG. 2. Magnetization vs temperature curve for the compound $La_{1-x}Zr_xMnO_3$ ($x=0.05-0.20$) at a field of 1000 G. The inset shows the detail of the curves around T_C.

perimental and calculated XRD pattern for $La_{0.90}Zr_{0.10}MnO_3$ compound. The lattice parameters were obtained as $a=5.537$ Å and $c=13.365$ Å with a coordination number of six. The six Mn–O were determined to be 1.971 Å and the La–O bond length was obtained as 2.758 Å. This compression and extension of Mn–O and La–O bonds result in a deviation of tolerance factor from unity and comes out to be equal to 0.98. The resulting internal stress causes MnO_6 to rotate about [111] axis and bend the Mn–O–Mn bond angle from 180°.[10] In the present case the Mn–O–Mn bond angle was determined to be 162.44°. The distortion of the bond angle results in a change in the Mn d and O $2p$ orbital overlap thereby affecting the double exchange as well as the superexchange interaction.

Figure 2 shows the magnetization versus temperature curves for the compound $La_{1-x}Zr_xMnO_3$ ($x=0.05-0.20$). A sharp ferromagnetic to paramagnetic transition is observed for all the compounds. A little anomaly seen at a temperature of 43 K is attributed to the Mn_2O_3 impurity phase. The transitions are sharp and take place within a narrow temperature window. The transition temperature increases for $0.05 \leqslant x \leqslant 0.07$ but stabilizes for higher values of x and increases very slowly. The T_C values are obtained as 202, 233, 235, 233, and 236 K for $x=0.05$, 0.07, 0.10, 0.15, and 0.20, respectively. The saturation of T_C may be attributed to a competition between the double exchange and the core spin interaction. When x amount of Zr^{4+} is doped in $LaMnO_3$ an equivalent amount of Mn^{3+} gets converted to Mn^{2+}. Since for Mn^{2+} there is no crystal field splitting so instead of e_g and t_{2g} orbital now there is d^5 orbital with five electrons. The relevant interactions then are e_g-t_{2g}, e_g-d^5, and $t_{2g}-d^5$ interactions. At low doping levels the Hunds coupling is strong and the e_g spin is determined by both e_g-t_{2g} and e_g-d^5 interaction. Thus, the ferromagnetism is mainly due to double exchange interaction and there is a T_C variation. At high doping limits ($x \geqslant 0.07$) the e_g-d^5 interaction is strong in comparison to e_g-t_{2g} levels and competes with $t_{2g}-d^5$ interactions and so canting of the spins take place[11] resulting in a nonvanishing ferromagnetic component. Above $x=0.07$, the Hund coupling become weak so that the variation of transition temperature with bandwidth is small and may change little with change in Mn–O–Mn bond angle.[12]

The resistivity versus temperature curves is shown in Fig. 3. The compounds show smooth variation from low conductivity to high conductivity with increasing Zr content. There is an increase of residual resistivity with decreasing Zr content. A small anomaly seen for $La_{0.80}Zr_{0.20}MnO_3$ may be

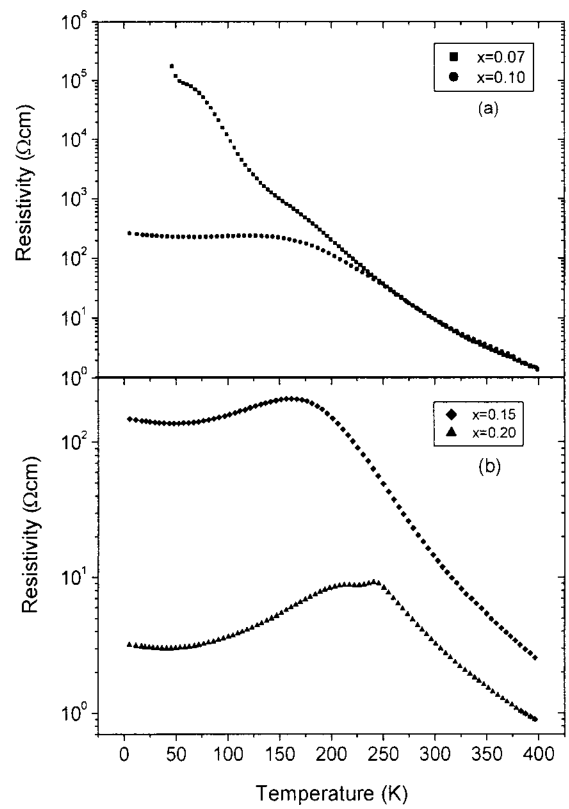

FIG. 3. Zero field resistivity vs temperature curve for the compound $La_{1-x}Zr_xMnO_3$ ($x=0.07-0.20$).

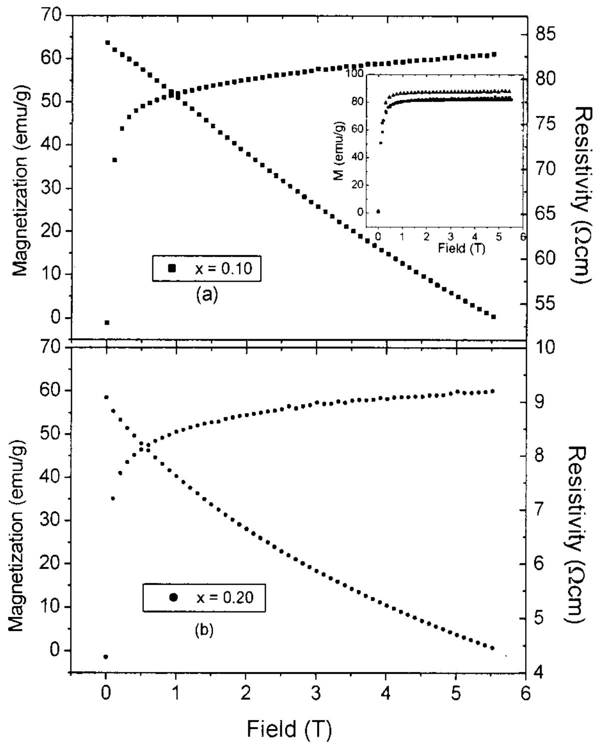

FIG. 4. Magnetization and resistivity vs field curve for $La_{1-x}Zr_xMnO_3$, $x = 0.10$ and 0.20 at a temperature of 210 and 230 K, respectively. The inset in (a) shows the magnetization vs field for $x = 0.07$, 0.10, and 0.15 compound measured at 10 K.

due to an impurity phase. Unlike the magnetization curves the resistivity shows a variation of the metal–insulator transition temperatures T_{im}. Thus, ferromagnetism alone cannot explain charge transport and other effects like orbital ordering need to be taken into account. Compounds with $x < 0.10$ show insulating behavior while for $x \geqslant 0.10$ the metallic and insulating region is separated by a distinct resistive peak. The T_{im} values are obtained as 125, 160, and 210 K for $x = 0.10$, 0.15, and 0.20, respectively. The increase of conductivity with increasing Zr content is due to an increased Mn^{2+}/Mn^{3+} ratio. But since there is no vacancy in the Mn^{2+} site so only the e_g electron due to Mn^{3+} is the charge carrier in this case. This along with the fact that electrons have a higher tendency of localization explains the high residual resistivity of these compounds. The other fact to be noted is that with increasing Mn^{2+} content there is an increase in d^5 orbital that gives rise to a difference in the number of Jahn–Teller active and Jahn–Teller inactive states. These states hybridize differently with O $2p$ states and so there is rearrangement of the orbitals that may give rise to orbital ordering effect. With increased doping the $e_g - t_{2g}$ interaction become weak and $e_g - d^5$ interaction grows. This makes the electron hopping term increase so that the overall resistivity decreases.

The variation of magnetization and the resistivity with magnetic field for $x = 0.10$ and 0.20 compounds is shown in Fig. 4. The increase of magnetization is very sharp at lower fields while at higher fields the rate of increase is much slower. On the other hand the resistivity decreases at a faster rate at 5 T. This means that the resistivity has other origin apart from spin scattering. One common situation in polycrystalline compounds is the scattering due to grain boundaries.[13] The spin alignment crucially affects the resistivity and even high fields are not enough to saturate the resistivity. The grain boundaries can have a short range antiferromagnetic interaction that acts as scattering sites. Even at high fields the intergrain spins are not aligned and so the resistivity is not saturated. The magnetoresistance $[\Delta\rho/\rho(0)]$ is 36% and 50% for the $x = 0.10$ and $x = 0.20$ compound. The inset of Fig. 4(a) shows the magnetization versus field curve for $x = 0.07$, 0.10, and 0.15 compounds at 10 K. The saturation magnetization for $x = 0.10$ compound is 83.56 emu/g or 0.042 μ_B. Such high magnetization value is probably due to half filled d orbital present in the system due to Mn^{2+}.

ACKNOWLEDGMENT

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