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Pressure effects on the transport and magnetic properties of $La_{1.4}Sr_{1.6}Mn_2O_7$

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The effects of external (hydrostatic) pressure and internal (chemical) pressure on the transport and magnetic properties of the $La_{1.4}Sr_{1.6}Mn_2O_7$ are investigated. Both metal-insulator transition temperature T_m and Curie temperature T_C increase with the increase of external pressure. In contrast, the T_m and T_C decrease with the increase of Ca content in $La_{1.4}(Sr_{1-x}Ca_x)_{1.6}Mn_2O_7$ $(x\leqslant 0.3)$, where the internal pressure is supposed to be introduced. External pressure enlarge the ferromagnetic metal phase through the pressure-enhanced transfer interaction of the charge carriers. The Mn-O-Mn bond angle remains almost unchanged with the increase of Ca content which is in sharp contrast to the $La_{1-x}Sr_xMnO_3$ system. The Mn-O(3) bond length is decreased by the external pressure while increased by the internal pressure. It is interpreted that the opposite behaviors of T_m and T_C for external and internal pressures are due to the different variations of Mn-O(3) bond length. All other results are discussed and compared with those in the (La,Sr)MNO_3 system. [S0163-1829(98)06642-9]

I. INTRODUCTION

The discovery of huge negative magnetoresistance, now termed colossal magnetoresistance (CMR), in the doped manganites $(R,A)MnO_3$ ($R=$La, Pr, Nd, etc.; $A=$Ca, Sr, Ba, Pb) with a perovskite structure has become a subject of intense interest.[1–4] The increased interest in the study of these systems arises from the high correlation between their structural, transport, and magnetic properties at T_C, the Curie temperature.[5,6] Recently, large magnetoresistance has been observed in other crystal structures, namely, the pyrochlore $Tl_2Mn_2O_7$ (Refs. 7 and 8) and layered $(Nd,Sr)_3Mn_2O_7$.[9] The $(La,A)_3Mn_2O_7$ is a member of the family $(La,A)_{n+1}Mn_nO_{3n+1}$ (A is the alkaline earth metal), where n is the number of perovskite layers. In this paper we have chosen the $La_{1.4}Sr_{1.6}Mn_2O_7$ composition (in which the $Mn^{4+}/Mn^{3+}=3/7$) for our investigation, because in the $La_{0.7}Sr_{0.3}MnO_3$ system T_C is maximum for the same value of Mn^{4+}/Mn^{3+} $(=3/7)$.

Moritomo, Asamitsu, and Tokura[10] reported that high pressure, which effectively increases the electron transfer interaction or the one-electron bandwidth W, is a powerful tool for investigation of the electronic and magnetic properties of strongly correlated $3d$-electron systems. Application of pressure affects the electronic properties, especially near the insulator-metal (IM) phase boundary.[11–14] In an extreme case, a pressure induced metallic phase persists down to zero temperature, as demonstrated in the $PrNiO_3$ (Refs. 11, 12) and V_2O_3.[13] In this class of compounds, the pressure increased itineracy of the carriers is expected to influence the magnetic properties as well. One of the demonstrative examples is the pressure effect on a prototypical Mott insulator $LaTiO_{3+\delta/2}$.[15] The application of pressure increases the Néel temperature T_N in a filling ($n=1-\delta$, where n is the band filling and δ is the hole concentration) dependent manner, suggesting a crossover behavior from localized to itinerant magnetism with increasing δ. Important quantities that govern the electronic as well as magnetic properties are the one-electron bandwidth (W) of the e_g band and the on site exchange interaction (Hund coupling; J) between the itinerant e_g electron and the local t_{2g} spin.[1,16] Another important parameter in these perovskites (ABO_3) is the average ionic radius of the A site, $\langle r_A\rangle$. In several perovskites, the overlap between B-site d orbitals and oxygen p orbitals forms the electronically active band and this overlap can be strongly influenced by the internal pressure generated by A-site substitution with ions of different radii.[17] On the other hand, Mn-O-Mn bond angle also plays a crucial role in the $(La,A)MnO_3$ compounds[18,19] and which is in the 155°–170° range in these perovskites.[20,21] Argyriou *et al.* reported that Mn-O-Mn bond angle in $La_{1.2}Sr_{1.8}Mn_2O_7$ is about 180° and it does not change with hydrostatic pressure.[22] Very recently, Kimura, Asamitsu, Tomioka, and Tokura[23] have studied the external pressure effect on the magnetic and transport properties of the same composition ($La_{1.4}Sr_{1.6}Mn_2O_7$) and they have discussed that the application of pressure weakens the interplane magnetic coupling. Therefore it will be interesting to study the effects of internal pressure on the bond length and bond angle, subsequently, on the electrical and magnetic properties of $La_{1.4}Sr_{1.6}Mn_2O_7$ and compared to those carried out by external pressure. Here, the internal pressure is introduced by doping Ca on the Sr site, i.e., by changing $\langle r_A\rangle$, keeping Mn^{4+}/Mn^{3+} ratio fixed.

II. EXPERIMENTAL DETAILS

$La_{1.4}(Sr_{1-x}Ca_x)_{1.6}Mn_2O_7$ $(0\leqslant x\leqslant 0.3)$ samples were prepared by standard solid-state reaction method. Stoichiometric

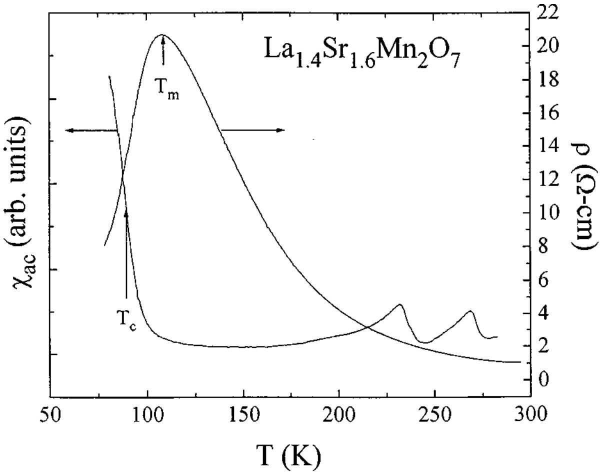

FIG. 1. Temperature variations of the ac susceptibility (χ_{ac}) and resistivity (ρ) of the $La_{1.4}Sr_{1.6}Mn_2O_7$ sample. T_m and T_C are, respectively, the metal-insulator transition temperature and Curie temperature. We have defined the inflection point of the χ_{ac}-T curve as T_C.

mixtures of high-purity oxides La_2O_3, $SrCO_3$, $CaCO_3$, and MnO_2 were first calcined in air at 900 °C for 12 h, and reground and fired in air at 1200 °C for 12 h. Then, the obtained powder was pressed into pellets and sintered in air at 1400 °C for 24–48 h with intermediate grindings for three times. Powder x-ray diffraction data were obtained using SIEMENS D5000 diffractometer with Cu $K\alpha$ radiation at room temperature. Structural parameters were refined by the Rietveld method, using the program GSAS.[24] The resistivity was measured on samples of rectangular parallelepipeds of approximate dimensions $0.5\times2\times7$ mm^3 using standard four-probe method. ac magnetic susceptibility was measured by mutual induction method using low frequency (~30 Hz). Data on the hydrostatic pressure dependence of resistivity and ac magnetic susceptibility in $La_{1.4}Sr_{1.6}Mn_2O_7$ were taken up to 17 kbar using the piston cylinder self-clamped technique. 3M inert fluid was used as pressure transmitting fluid with superconducting Pb manometer. In each instance, the original value was reproduced after the pressure released within experimental error indicating complete reversibility of the pressure effect.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the temperature variations of resistivity and ac susceptibility of the $La_{1.4}Sr_{1.6}Mn_2O_7$ sample. It is found that, with decreasing temperature resistivity increases and becomes maximum at a temperature, T_m (108 K), where T_m is denoted as metal-insulator transition temperature. When the temperature is further decreased below T_m, the resistivity also decreases. In the temperature variation of ac susceptibility (χ_{ac}) curve, two small peaks are found between 200 and 300 K. With further decrease of temperature a transition from paramagnetic to ferromagnetic occurs. We have defined the inflection point of the χ_{ac}-T curve as T_C (90 K), the Curie temperature. The electrical and magnetic properties of this $La_{1.4}Sr_{1.6}Mn_2O_7$ compound can be basically understood on the basis of double exchange interaction theory.[25,26] According to this theory, these magnetic manganese oxide compounds have $Mn^{3+}$and Mn^{4+} ions and these ionic states fluctuate due to electron transfer between them. As a result of this electron transfer, antiferromagnetically ordered manganese spins cant, and both magnetization and metallic conductivity appear simultaneously. The magnetization increases as the canting angle (an antiparallel alignment of moments in the antiferromagnetic state has been taken as zero canting) decreases.[27] The two small peaks appeared in 200–300 K of the ac susceptibility curve for the present $La_{1.4}Sr_{1.6}Mn_2O_7$ compound are consistent with those observed by MacChensey, Potter, and Sherwood[28] in $La_{1.33}Sr_{1.66}Mn_2O_7$ polycrystalline sample and by Mitchel *et al.*[29] in $La_{1.2}Sr_{1.8}Mn_2O_7$ single crystal. MacChensey, Potter, and Sherwood speculated that spin correlation above T_C might be intrinsic to this class of two-dimensional materials. Moritomo *et al.*[30] likewise claimed that two-dimensional spin correlation is responsible for the moment they observed in $La_{1.2}Sr_{1.8}Mn_2O_7$ single crystal at temperature above T_C. It is to be noted that these small peaks are absent in dc susceptibility with applied field 1 kOe in the present $La_{1.4}Sr_{1.6}Mn_2O_7$ system. So, these peaks might be due to the short range or very weak canting ordering.

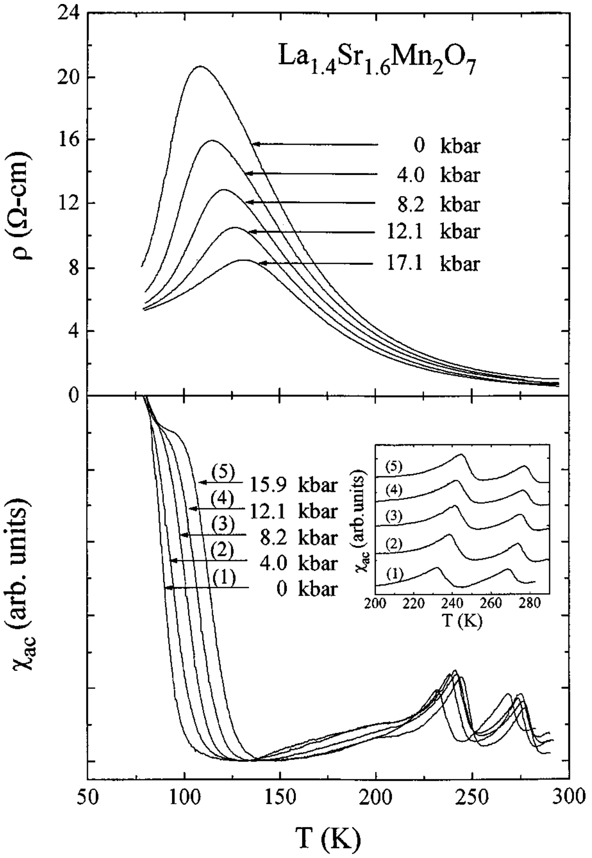

FIG. 2. Temperature variations of resistivity (upper panel) and ac susceptibility (lower panel) of the $La_{1.4}Sr_{1.6}Mn_2O_7$ sample under different hydrostatic pressures. Inset: pressure effect on the small peaks found in the ac-susceptibility curve between 200 and 300 K.

The temperature variations of resistivity and ac susceptibility of $La_{1.4}Sr_{1.6}Mn_2O_7$ with different pressures are shown in Fig. 2. It is found that with increasing pressure, both $T_m$and T_C increase and the electrical resistivity decreases. This illustrates that the application of pressure enlarges the ferromagnetic metal phase through the pressure enhanced transfer interaction of the charge carriers. Moritomo,

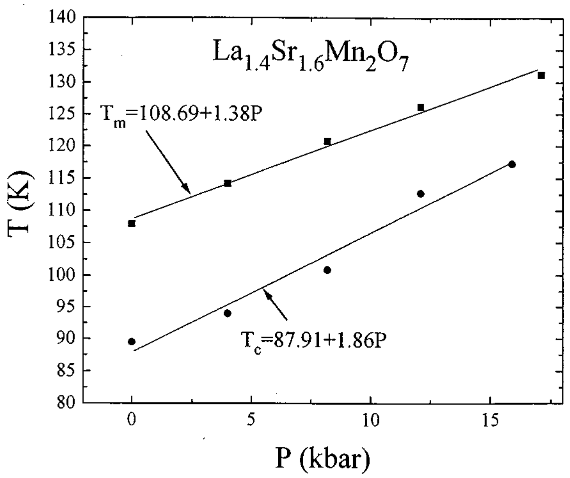

FIG. 3. The variations of T_m (■) and T_C (●) of the $La_{1.4}Sr_{1.6}Mn_2O_7$ sample with external pressure (P). The lines are the linear fits to the data points.

Asamitsu, and Tokura[10] and Itoh *et al.*[31] found the similar positive pressure effect on the $La_{1-x}Sr_xMnO_3$ compounds. The variations of T_m and T_C of the $La_{1.4}Sr_{1.6}Mn_2O_7$ compound with pressure are shown in Fig. 3. The T_m and T_C are fairly linear with applied pressure P in the studied range $\leqslant 17$ kbar. The pressure coefficient ($d \ln T_C/dP$) estimated from the slope in Fig. 3 is about 0.018 $kbar^{-1}$.This pressure coefficient is larger than that observed by Moritomo, Asamitsu, and Tokura[10] for the $La_{1-x}Sr_xMnO_3$ which varies from 0.0005 to 0.0065 $kbar^{-1}$ depending on the hole concentration (x) and with increasing x the pressure coefficient decreases. This is in reasonable agreement with that observed by Laukhin *et al.*[32] that the samples having higher T_C are less sensitive to pressure than those of lower T_C. The small peaks in the ac susceptibility curve of the present system also shifted towards higher temperature with increasing pressure (shown in the inset of Fig. 2). It is worth mentioning that the values of $d \ln T_C/dP$ and $d \ln T_m/dP$ are somewhat different (Fig. 3). It may suggest that the double exchange interaction cannot completely explain both the metal-insulator and ferromagnetic-paramagnetic transitions in $La_{1.4}Sr_{1.6}Mn_2O_7$.

In order to study the chemical pressure effect on $La_{1.4}Sr_{1.6}Mn_2O_7$ compound, $La_{1.4}(Sr_{1-x}Ca_x)_{1.6}Mn_2O_7$ with $x = 0.0$, 0.1, 0.2, and 0.3, samples are synthesized and characterized by powder x-ray diffraction. The diffraction patterns shown in Fig. 4 indicate clean single phase as $x \leqslant 0.3$. Figure 5 shows the variation of the lattice parameters a, c, and volume V with Ca content. The decrease of a, c, and V with x in $La_{1.4}(Sr_{1-x}Ca_x)_{1.6}Mn_2O_7$ following Vegard's law indicates the same crystal structure for the four studied compounds. Figure 6 shows the temperature variations of resistivity and ac susceptibility of the $La_{1.4}(Sr_{1-x}Ca_x)_{1.6}Mn_2O_7$ for $x = 0$, 0.1, 0.2, and 0.3. With increasing Ca content, the T_C and T_m values decrease. It is also found from Fig. 6 that $\rho(T)$ above the transition is virtually identical for all the samples, the only difference being that the magnitude slowly increases with increasing Ca content. This suggests that the nature of charge transport in the nonmetallic state above T_m is almost the same. In both Figs. 2 and 6 it is found that the higher the T_C, the higher the conductivity. This means that the metallic and ferromagnetic properties originate mainly

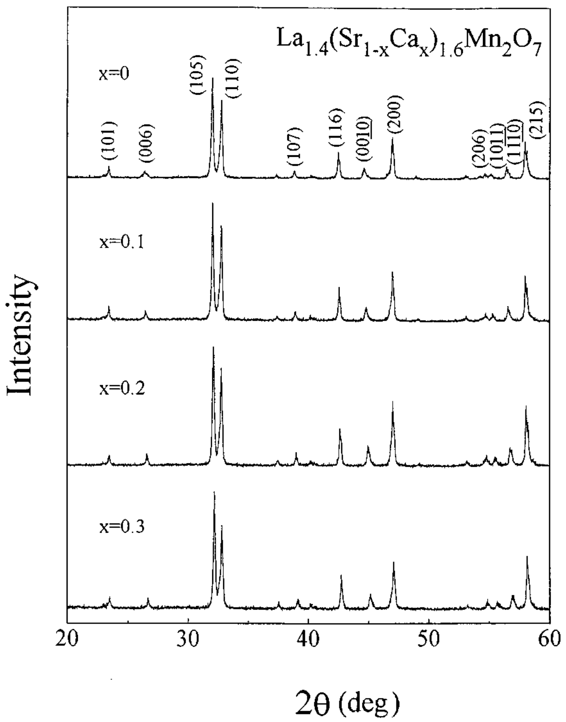

FIG. 4. X-ray diffraction pattern for the $La_{1.4}(Sr_{1-x}Ca_x)_{1.6}Mn_2O_7$ system with $x = 0$, 0.1, 0.2, and 0.3. The Miller indices refer to the space group *I*4/*mmm*.

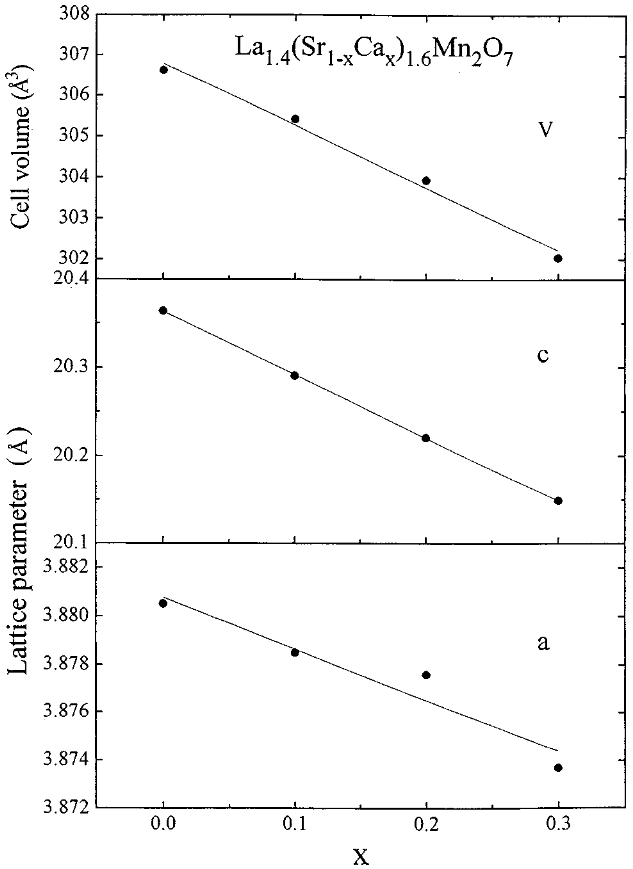

FIG. 5. The variations of lattice parameters (a,c) and cell volume (V) with Ca content x. The lines are guides to the eye.

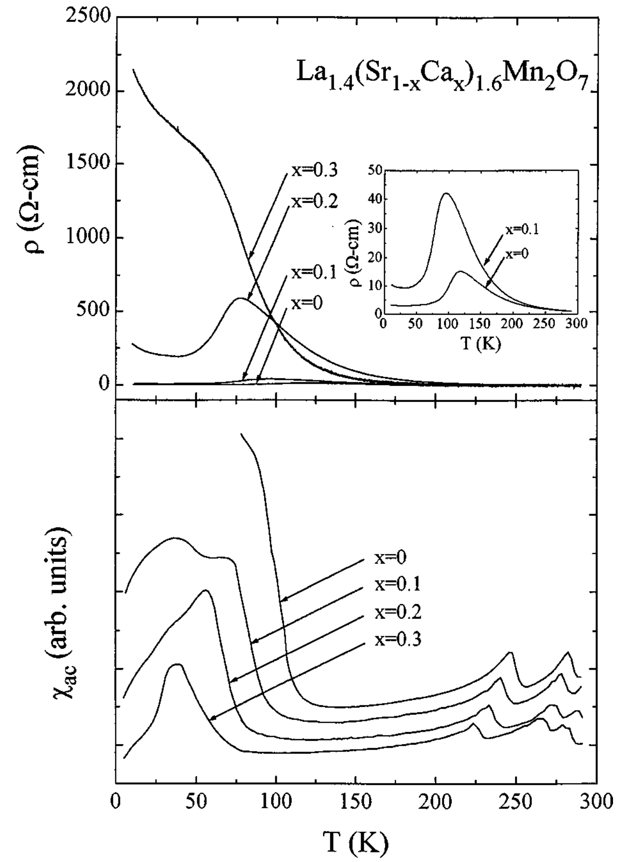

FIG. 6. Temperature variations of resistivity (upper panel) and ac susceptibility (lower panel) of the $La_{1.4}(Sr_{1-x}Ca_x)_{1.6}Mn_2O_7$ system with $x=0$, 0.1, 0.2, and 0.3. Inset: temperature variations of resistivities for $x=0$ and 0.1 are shown in extended scale.

from the same physical mechanism. Several groups[18,33,34] have already studied the variations of magnetic and transport properties at constant doping level by varying the *A*-site cation composition in the (La,Sr)MnO_3 system. Hwang *et al.*[19] also observed that T_C decreases with increase of Pr content in the $La_{0.7-x}Pr_xCa_{0.3}MnO_3$ and Y content in the $La_{0.7-x}Y_xCa_{0.3}MnO_3$ compounds. From all the studies,[18,19,33,34] it is found that a metal-insulator transition can be induced by decreasing the average *A*-site ionic radius $\langle r_A\rangle$. T_C varies by more than a factor of 2 as a function of $\langle r_A\rangle$, and for the Mn^{4+}/Mn^{3+} ratio of 3/7, it displays a maximum corresponding to the composition $La_{0.7}Sr_{0.3}MnO_3$. This effect has been discussed by majority of the authors in terms of a variation of electronic bandwidth *W* as a function of chemical pressure, with the main focus being on the influence of Mn-O-Mn bond angle on *W*. The Mn-O-Mn bond angle decreases as a function of decreasing $\langle r_A\rangle$, which would account for the general trend of decreasing T_C with this parameter (the metallic phase is stabilized with larger values of *W*). It is also found that the smaller peaks in ac susceptibility curve (Fig. 6) are shifted towards lower temperature with increasing the internal pressure. The variations of T_m and T_C with Ca content are shown in Fig. 7. Similar to Fig. 3, these variations are not exactly parallel to each other.

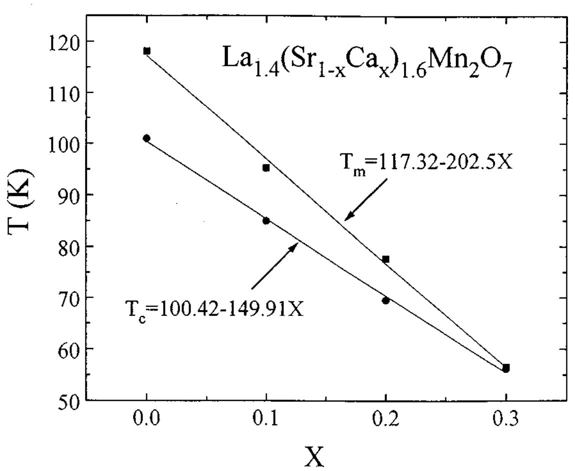

FIG. 7. The variations of T_m (■) and T_C (●) of the $La_{1.4}Sr_{1.6}Mn_2O_7$ sample with Ca content *x*. The liens are the linear fits to the data points.

We can explain the T_C variation of the present system based on the reduction of *W* with the increase of Ca content. For perovskite compounds with general formula ABO_3, it is a straightforward result from tight-binding approximation that *W* depends on both the *B*-O-*B* bond angles and *B*-O bond lengths, through the overlap integrals between *3d* orbital of the metal ion *B* and the *2p* orbital of the O anion. The following empirical formula has been used to describe the double dependence:[35]

$$W \propto \cos\omega/(d_{B\text{-O}})^{3.5}, \qquad (1)$$

where $\omega=\frac{1}{2}(\pi-\langle B\text{-O-}B\rangle)$and $d_{B\text{-O}}$ is the *B*-O bond length. In our case *B* stands for Mn. Assuming that T_C is very sensitive to small *W* variations, Radaelli *et al.*[18] have found that *W* is solely responsible for the metal-insulator transition. From the refinement data of the present Ca doped system, it is found that with increase of Ca content, the average Mn-O-Mn bond angle remains almost unchanged (Fig. 8). Similar phenomena have been observed in the $La_{1.2}Sr_{1.8}Mn_2O_7$ system where external pressure was introduced.[22] This is in contrast to the $La_{1-x}Sr_xMnO_3$ system where application of both external pressure and internal pressure changes Mn-O-Mn bond angle.[18] Moreover, the value of bond angle observed from refinement data is about 180° which implies that in $La_{1.4}(Sr_{1-x}Ca_x)_{1.6}Mn_2O_7$ size match is perfect. This can also be verified from the ''tolerance factor'' calculation. It is a geometrical quantity defined as $t'=(d_{A\text{-O}})/\sqrt{2}(d_{\text{Mn-O}})$. The factor t' is a simple characterization of the size mismatch that occurs when the *A*-site ions are too small to fill the space in the three-dimensional network of MnO_6 octahedral. For a perfect size match $t'=1$. From the refinement analysis we have obtained the average $d_{A\text{-O}}=2.669$ Å, 2.645 Å, 2.683 Å, and 2.615 Å, and the average $d_{\text{Mn-O}}=1.96$Å, 1.989 Å, 1.988 Å, and 2.043 Å, respectively, for $x=0$, 0.1, 0.2 and 0.3. For $x=0$ sample (in which case $d_{A\text{-}O}=2.669$ Å and $d_{\text{Mn-O}}=1.96$ Å) the value of t' is estimated to be 0.963. For the other samples also the value of t' is nearly 1. Figure 8 also shows that the average Mn-O bond length increases with the increase of Ca content (chemical pressure) in the present $La_{1.4}Sr_{1.6}Mn_2O_7$ system. This is similar to that observed in $La_{1-x}Sr_xMnO_3$.[18] The effect of increasing Mn-O bond length is to decrease *W*. It has already been mentioned that according to the double exchange model, the double exchange interaction is proportional to *W*. Therefore, as *W* decreases, the double exchange interaction also decreases

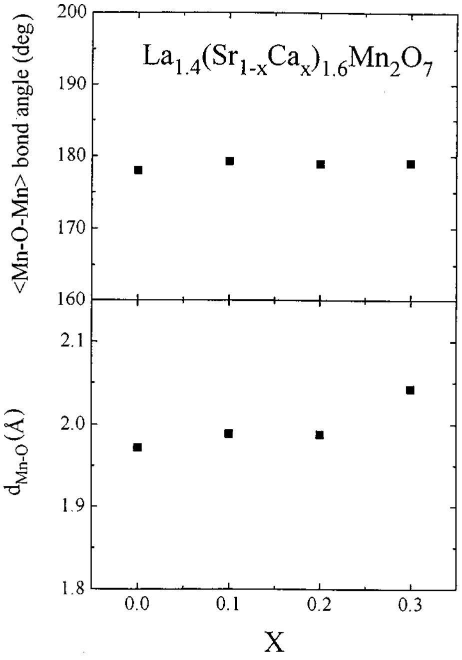

FIG. 8. The variations of average Mn-O bond length and Mn-O-Mn bond angle, which are derived from Rietveld analysis for $La_{1.4}(Sr_{1-x}Ca_x)_{1.6}Mn_2O_7$ with x at room temperature.

and as a consequence T_C of the present $La_{1.4}(Sr,Ca)_{1.6}Mn_2O_7$ system decreases.

To discuss more specifically, we have shown the variations of different bond lengths with Ca content (chemical pressure) of the present $La_{1.4}(Sr_{1-x}Ca_x)_{1.6}Mn_2O_7$ in Fig. 9. It is found that with increase of chemical pressure Mn-O(1) bond length decreases and Mn-O(2) bond length increases which is similar to those observed in $La_{1.2}Sr_{1.8}Mn_2O_7$ compound where external pressure was introduced.[22] But, in $La_{1.2}Sr_{1.8}Mn_2O_7$ compound Mn-O(3) bond length decreases with the increase of external pressure, whereas in the present case Mn-O(3) bond length increases with the increase of internal pressure. Therefore, the opposite behaviors of external pressure effect and chemical pressure effect should be due to the fact that Mn-O(3) bond length decreases with the increase of external pressure whereas it increases with the increase of chemical pressure.

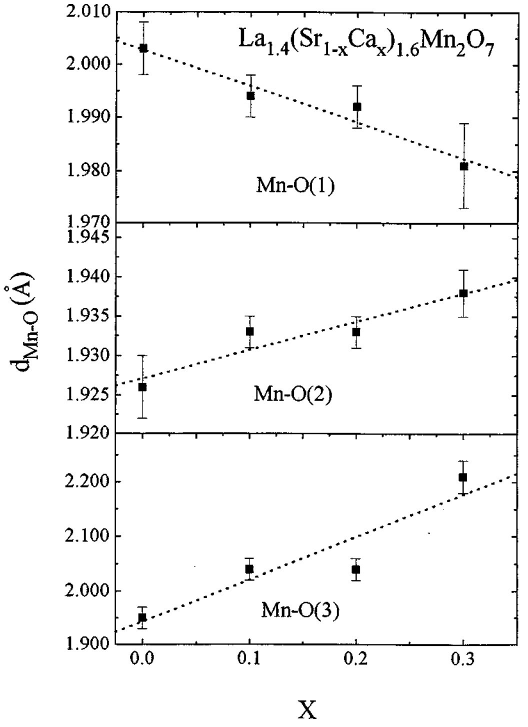

FIG. 9. The variations of Mn-O bond lengths in $La_{1.4}(Sr_{1-x}Ca_x)_{1.6}Mn_2O_7$ with Ca content at room temperature. Lines are weighted least-squares fits to the data.

We have already mentioned that the external pressure (internal pressure) increases (decreases) the T_m and T_C at the slightly different rate (Figs. 3 and 7). If double exchange interaction is the only origin of both metal-insulator and ferromagnetic-paramagnetic transitions, rates of the variations of T_m and T_C with pressure are supposed to be exactly equal. Therefore, other than the double exchange mechanism, the possibility of some other minor reasons should be considered. Moreover, according to the most recent theoretical discussion, it appears that, in addition to W, another energy scale acts as an essential ingredient in the description of this system, namely the Jahn-Teller energy T_{JT}. For instance, Millis, Shraiman, and Mueller[36] have proposed a generalized phase diagram of the manganites at constant doping $x \sim 0.3$, as a function of reduced temperature T/t (t is the electron hopping parameter, which is proportional to W), and of the electron-phonon coupling $\lambda = E_{JT}/t$. Therefore, possible variation of E_{JT} as a function of chemical or external pressure effect cannot be ruled out.

IV. CONCLUSION

We have studied the external and the chemical (internal) pressure effects on the resistivity and the ac susceptibility of the $La_{1.4}Sr_{1.6}Mn_2O_7$ sample. Both T_m and T_C increase with the external pressure but decrease with chemical pressure which is introduced by Ca doping in $La_{1.4}(Sr_{1-x}Ca_x)_{1.6}Mn_2O_7$. It is found that the higher the T_C the higher the conductivity which implies that metallic and ferromagnetic properties originate mainly from the same physical mechanism. With the increase of Ca content in $La_{1.4}(Sr_{1-x}Ca_x)_{1.6}Mn_2O_7$ (x up to 0.3), the average Mn-O-Mn bond angle remains almost unchanged in contrast to that in $La_{1-x}Sr_xMnO_3$ where application of both external pressure and internal pressure change Mn-O-Mn bond angle.[29] Comparing the variations of Mn-O bond lengths with the chemical pressure [doping Ca in $La_{1.4}(Sr_{1-x}Ca_x)_{1.6}Mn_2O_7$] and with the external pressure in $La_{1.2}Sr_{1.8}Mn_2O_7$,[22] it is concluded that the opposite external pressure and internal pressure effects on T_M and T_C might be due to the fact that Mn-O(3) bond length decreases when external pressure is introduced but increases with internal pressure. The metal-insulator and paramagnetic-ferromagnetic transitions can be explained fairly well with the double exchange interaction between Mn^{3+} and Mn^{4+}. But, it cannot fully explain the variations of T_m and T_C (though the difference is small) with external and internal pressure at different rates. Therefore some other minor origins need also be considered.

ACKNOWLEDGMENT

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