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VOLUME-BASED CONSIDERATIONS FOR THE METAL-INSULATOR TRANSITION OF CMR OXIDES

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ABSTRACT

The sensitivity of $\rho$ to changes in volume which occur through: (1) applied pressure, (2) variations in temperature, and (3) phase transitions, is evaluated for some selected CMR oxides. It is argued that the changes in volume associated with phase changes are large enough to produce self pressures in the range of 0.18 to 0.45 GPa. The extreme sensitivity of the electrical resistivity to pressure indicates that these self pressures are responsible for large features in the electrical resistivity and are an important component for occurrence the metallicity below $T_c$. It is suggested that this is related to a strong volume dependence of the electron phonon coupling in the CMR oxides.

INTRODUCTION

Ferromagnetic transition metal oxides of the chemical composition $A_{1-x}\tilde{A}_x\text{MnO}_3$ (where $A =$ La, Pr, Gd, Pb, Nd and $\tilde{A} =$ Ca, Sr, Ba, Cd) have been investigated since the early 1950's [1-2]. At the ferromagnetic transition temperature $T_c$ the electrical resistivity displays a metal-insulator transition. This is quite different from common metallic ferromagnets for which the electrical resistivity exhibits a modest change in slope at $T_c$ due to a decrease of spin-disorder scattering as ferromagnetism sets in. Zener [3] proposed an explanation for the ferromagnetic interaction called double exchange (DE). In the double exchange picture, electrical conduction can occur only if neighboring Mn ions are ferromagnetically aligned. The conduction lowers the ground-state energy of the system and mediates the ferromagnetic exchange.

The interplay between magnetic, structural, and electrical transport properties in this system is exceptionally strong, and leads to the largest negative magnetoresistivity (MR) observed in any material near room temperature; the effect is often referred to as colossal magnetoresistance (CMR). If one defines $\text{MR} = |\rho(H) - \rho(0)|/\rho(0)$, it can have a magnitude larger than 90% [4-8]. This exceedingly large MR opens the door for a number of potential applications of $A_{1-x}\tilde{A}_x\text{MnO}_3$ in sensor technology. In addition to the technological promise of the CMR oxides, they provide an example of how subtle aspects of the crystal structure play an important role in determining the electrical and magnetic properties of complex oxides.

A number of diverse experiments indicate that conduction in CMR materials takes place via magnetic polarons. A magnetic polaron consists of a conducting hole and a group of magnetic spins which propagates through the lattice by aligning neighboring spins along its path. Diffuse magnetic scattering of neutrons above $T_c$ displays an activation energy consistent with that observed in electrical resistivity measurements [9], in support of electrical conduction via magnetic polarons. Measurements of thermoelectric power [10,11] and electrical resistivity [8] illustrate that the energy gap determined by electrical resistivity measurements is about 10 times larger than that determined by thermoelectric power, this is considered the hallmark of conduction via polarons. Local structure analysis of powder neutron diffraction data [12] and x-ray...
absorption measurements [13,14] reveal local structural distortions which are consistent with lattice polaron formation. Thus, a reasonable scenario is that the polarons manifest themselves as both a magnetic and lattice distortion. Theoretical investigation has noted that the DE model alone cannot explain the large MR [15] and the significance of magnetic polarons as well as the structural distortion associated with the Jahn-Teller effect [15-17]. Thus, both experimental and theoretical investigations indicate that lattice distortions, presumably associated with magnetic polarons, play an important role in determining the properties of CMR materials.

The formation of polarons in the manganese oxides is a result of large electron-phonon coupling [18]. The polarons disappear as T is decreased below Tc, thus permitting formation of the metallic state. The significance of electron-phonon coupling for the ferromagnetic exchange has been demonstrated by the observation of a large oxygen isotope effect on Tc [19]. In addition, a series of high pressure experiments on specimens where the structure has been altered by chemical substitution indicates that electron-phonon coupling plays an important role in the influence of pressure on Tc and the electrical resistivity [20].

The focal point of this work is the thermodynamic properties of the CMR materials. These experiments deal with measurements of chemical compositions at the boundary between ferromagnetic metal and ferromagnetic insulator [21]. The sensitivity of CMR materials to pressure (i.e. a controlled reduction of the volume) is examined to evaluate the influence of temperature-dependent volume changes on the electrical resistivity.

EXPERIMENTAL

A 10 g polycrystalline specimen of La0.79Ca0.21MnO3-y was prepared from 99.99% purity La2O3 (dried at 600 °C), CaCO3, and MnO2 which were mixed and reacted at 1100 °C in air for 20 h. The specimen was always removed from the furnace at T > 1000 °C to reduce the number of La vacancies σ that form by the uptake of oxygen [22]. After the initial reaction, the powder was reground, reacted at 1200 °C for 20 h, reground and reacted at 1350 °C for 20 h. The specimen was then reground, pelletized, and reacted at 1350 °C for 20 h; this step was repeated once. After regrounding, it was pressed, reacted at 1375 °C for 40 h, removed from the furnace at 1200 °C, and labeled specimen A (or simply A). A portion of this specimen (specimen B or B) was heated in air to 1375 °C and slow-cooled at 60 °C/h to 26 °C. Iodometric titration under the assumption of +3, +2, +2, and -2 valences for La, Ca, Mn, and O, respectively, in acidic solution yielded Mn valences of 3.239 ± 0.004 (σ = 9.70x10^-3 vacancies/formula-unit) for A and 3.266 ± 0.004 (σ = 18.7x10^-3 vacancies/formula-unit) for B. A monoclinic cell was used for lattice parameter calculations based on powder x-ray diffraction data with a Si standard yielding a=3.890(2), b=3.889(2), c=3.880(2) and β=89.96(5) for A and a=3.888(2), b=3.885(2), c=3.877(2) β = 89.96(5) for B whose unit-cell volume is 0.25 % smaller than A. Four-probe electrical resistivity and ac magnetic susceptibility measurements at high pressure are described elsewhere [23]. Magnetization studies were conducted with a commercially available SQUID magnetometer. Thermal expansion measurements utilized a capacitive dilatometer. A single crystal specimen of La0.83Sr0.17MnO3 was grown using the optical float zone method. Polycrystalline feed and seed rods were melted in air at ambient pressure. Rotation rates of 50 rpm were used for the feed and seed and growth rates were 3-5 mm/h.

THERMODYNAMICS OF A SECOND-ORDER PHASE TRANSITION
When a system undergoes a second-order phase transition, its volume $V$ changes in a continuous fashion. In contrast, when a system experiences a first-order phase transition, $V$ is discontinuous at the phase transition. For a second-order phase transition, the derivative of $V$, the volume thermal expansion $\beta(T)$, is discontinuous at $T_c$. The continuity of the Gibb’s free energy and its first derivative leads to the Ehrenfest relation given by

$$\Delta \beta = \frac{\Delta C_p}{V_{\text{mol}} T_c} \left[ \frac{dT_c}{dP} \right],$$  \hspace{1cm} (1)

where $\Delta \beta$ is the discontinuity in $\beta(T)$, $\Delta C_p$ is the discontinuity in the specific heat at constant pressure, $V_{\text{mol}}$ is the molar volume, and $dT_c/dP$ is the derivative of the phase transition temperature as a function of pressure near $P = 0$ [24]. Thus, Equation (1) provides a clear relation among a number of experimentally determinable quantities. The Ehrenfest relation will allow us to analyze the ferromagnetic to paramagnetic phase transition in the CMR specimens to be investigated below.

**MAGNETIC AND ELECTRICAL PROPERTIES AT AMBIENT PRESSURE**

In Fig. 1 the magnetization $M$ at $H = 4000$ Oe in units of $\mu_B$/Mn-ion is plotted versus temperature for the $La_{0.79}Ca_{0.21}MnO_3$ specimens. $M$ versus $H$ at 5 K appears in the inset. Both specimens A and B are clearly ferromagnetic with magnetic saturation moments $M(5 \text{ K}, 35 \text{ kOe})$ of 3.95$\mu_B$/Mn-ion and 3.71$\mu_B$/Mn-ion for A and B, respectively. Arrott plots (i.e. $M^2$ vs $M/H$) of magnetization data taken above and below the ferromagnetic transition temperatures and electrical resistivity data yielded $T_c$ values of 188.1 K and 192.6 K for A and B, respectively. These observations illustrate that the magnetic properties of A and B are quite similar.

![Fig. 1. Magnetization versus temperature for A and B at H = 4000 Oe. In the inset, the magnetic moment at 5 K is plotted versus H.](image-url)
Fig. 2. Electrical resistivity versus temperature for Specimens A and B at ambient pressure. In the inset, the electrical resistivity (in arbitrary units) is plotted versus T-T_c for warming and cooling.

In Fig. 2 the electrical resistivity $\rho$ versus temperature for A and B is shown at ambient pressure. At $T_c$, A (the reduced specimen) does not exhibit a metal-insulator transition. Specimen B, on the other hand, exhibits a metal-insulator transition typical for CMR materials. Warming and cooling through the transition at 0.17 K/min revealed minimal hysteresis for A and B of 0.4 K and 1.0 K, respectively, as illustrated in Fig. 1. Although the magnetic properties of A and B at ambient pressure are similar, it is evident that they differ markedly in terms of electrical conduction for temperatures below $T_c$. At 4 K, the electrical resistivity of A is over 3 orders of magnitude larger than that of B! The larger magnetic saturation moment of A, revealed in Fig. 1, may result from strong Hund's coupling of the localized electrical carriers to the Mn-ions. The difference between A and B can be qualitatively appreciated if one considers the phase diagram of Schiffer et al. [21] wherein the calcium composition 0.21 resides near the phase boundary separating the ferromagnetic insulating state (FMI) from the ferromagnetic metallic state (FMM).

**INFLUENCE OF PRESSURE ON THE ELECTRICAL RESISTIVITY**

In Fig. 3, the influence of pressure on the electrical resistivity is presented. The dashed line displays the ambient pressure $\rho(T)$ for B; data at higher pressures for a similar specimen appear elsewhere [23]. Application of pressure to A dramatically decreases $\rho$ revealing curves comparable to those of B at ambient pressure. Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ displays a similar pressure-induced metal-insulator transition [25]. Releasing the pressure on A from $P = 1.5$ GPa restored the insulating behavior. Thus, pressure facilitates a reversible crossover from the FMI to the FMM regions of the Schiffer et al. phase diagram [21]. Furthermore, the pressure sensitivity of $\rho$ is largest in the ferromagnetic state for both specimens. The pressure dependence of $T_c$ is presented in the inset of Fig. 3, the solid symbols were determined from the feature in $\rho$ at $T_c$ while the open symbols were determined by ac magnetic susceptibility $\chi_{ac}$; the feature in $\rho(T)$ occurs slightly.
Fig. 3. Electrical resistivity $\rho$ versus temperature, solid lines are for A, dashed line is the ambient pressure curve for B. In the inset, $T_C$ versus pressure for A (triangles) and B (squares), filled symbols are from $\rho$ data, open symbols are from ac magnetic susceptibility. Straight lines have slopes of 7.79 K/GPa and 40.3 K/GPa for A and B, respectively.

below $T_C$ at ambient pressure. The pressure derivatives $dT_c/dP(P=0)$ from $\chi_{ac}$ for these two specimens differ dramatically. Specimen A exhibits $dT_c/dP(P=0) = 7.79$ K/GPa while B displays $dT_c/dP(P=0) = 40.3$ K/GPa; $dT_c/dP$ of B agrees with that reported earlier [23]. The slope $T_c(P)$ for A increases at pressures greater than 0.6 GPa and attains values comparable to those of B.

VOLUME THERMAL EXPANSION AT AMBIENT PRESSURE

In Fig. 4 ambient pressure measurements of the volume expansion $\delta V_T = (V(T)-V(0))/V(0)$ are displayed. As is readily apparent, the volume changes in a continuous fashion at $T_c$ for both specimens. As discussed above, this indicates that the phase transition is second-order in nature. However, the electrical resistivity data in Fig. 2 indicate that a modest hysteresis occurs near $T_c$. We suspect that the phase transition may possess a weak first-order component, perhaps associated with a minor change in crystal structure. At any rate, the hysteresis observed here is minimal compared to that reported for a specimen of Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ [25]. The volume thermal expansion coefficient $\beta(T) = d(\delta V_T)/dT$ is plotted in the inset. The solid lines are for specimen A while the dashed lines are for specimen B. The jump in $\beta$ associated with the ferromagnetic transitions are $\Delta\beta = 7.6 \times 10^{-6}$ K$^{-1}$ and $3.0 \times 10^{-5}$ K$^{-1}$ for specimens A and B, respectively; note the surprisingly large difference in the $\Delta\beta$ values. Since $T_c$ is comparable for A and B, and if $\Delta C_p$ is assumed to be similar [26], the Ehrenfest relation predicts a smaller value of $dT_c/dP$ for A. This is indeed observed in the inset of Fig. 3. $\Delta C_p$ values calculated with Eq. (1) (5.1 J/mole-K and 4.0 J/mole-K for A and B, respectively) are comparable to $\Delta C_p$ reported [27] for a La$_{0.9}$Ca$_{0.1}$MnO$_3$.
specimen ($\Delta C_p \equiv 4.1\ J/mole-K$). This simple analysis indicates that our observation, namely the large difference in $dT_c/dP$ (and $\Delta \beta$) between A and B, appears to be consistent with the thermodynamics of a second-order phase transition.

![Graph showing volume change ($\delta V_T$) versus temperature for Specimens A and B](image)

**Fig. 4.** $\delta V_T = \{V(T) - V(0)/V(0)$ versus temperature for A (solid line) and B (dashed line). In the inset, the thermal volume expansion $\beta = d(\delta V_T)/dT$ is plotted versus temperature.

**VOLUME AND ITS ROLE IN THE METAL-INSULATOR TRANSITION**

The data above illustrate that although specimen A and B are quite similar in terms of composition, their electrical properties at ambient pressure are dramatically different. The temperature dependence of $\delta V_T$ as well as the volume dependence of $T_c$ (i.e. $dT_c/dP$) are also dissimilar for these two specimens. If we consider Specimen A, a small reduction of volume (through the application of hydrostatic pressure) results in electrical properties similar to B and an increase in $dT_c/dP$.

To develop a better qualitative understanding of the data, the bulk modulus $B_M = -V(dP/dV)$ is needed to estimate the volume change $\delta V = \{V(0)-V(P)/V(0)$ resulting from a given pressure. A room-temperature value of $B_M = 182\pm18$ GPa was estimated [28]. If no phase transitions occur, $B_M$ should vary by about 1% for $0 < T < 300$ K [28]. Resonant ultrasound measurements (RUS) [29] of a La$_{0.79}$Ca$_{0.21}$MnO$_{3-y}$ single crystal ($T_c = 295$ K) reveal $B_M(295$ K, $H=0) = 177 \pm 11$ GPa (in good agreement with our estimate), $B_M(270$ K, $H=0) = 138 \pm 8$ GPa, and $B_M(200$ K, $H=0) = 126 \pm 7$ GPa.

The importance of the subtle difference in crystallographic volume between A and B at room temperature can be appreciated through use of $B_M$. A given relative volume change $\Delta V/V$ is multiplied by $B_M$ to give the pressure which would be required to realize that volume change. At ambient pressure and 295 K the unit-cell volume of A is 0.25% larger than B, a pressure of 0.45 GPa would be required to reduce the volume of A to that of B at $P=0$; in fact, at this pressure A exhibits a M-I transition. This observation suggests that the contrast in temperature dependence of $\rho$ for A and B can be qualitatively attributed to the differing unit-cell volumes.
In considering the temperature dependence of the $\delta V_T$ curves, it is worthwhile to bring the data more into perspective through consideration of what is observed in a less exotic material. Consider copper which exhibits an expansion of $\delta V_T$ between 4 K and 300 K of about $9.6 \times 10^{-3}$, nearly a factor of two larger than what we observe for La$_{0.79}$Ca$_{0.21}$MnO$_{3-y}$ [30]. Furthermore, the bulk modulus of copper is 137 GPa [31] compared to our estimate of 182 GPa for the manganite. Thus the manganite is “harder” than copper (i.e. it take a larger pressure to realize a particular change in volume), and the changes in $\delta V_T$ with T are smaller. If the total change in $\delta V_T$ between 4 K and 300 K were multiplied by the respective bulk moduli for these two materials (as a normalization), the decrease in volume shown in Fig. 4 could be considered similar to that of copper.

Although the temperature-dependent volume effects are comparable to those of a common metal, a major difference exists in that $\rho(T)$ of the manganese oxides is particularly sensitive to pressure [20,23,25]. Thus, one might expect $\rho(T)$ to be influenced by temperature-dependent volume changes. Inspection of Fig. 4 indicates that specimen A, the poorly conducting specimen, exhibits a weak change in $\beta$ at the ferromagnetic transition temperature $T_c$. In contrast, specimen B exhibits a large change in $\beta$ at $T_c$.

In order to further evaluate the influence of the large change in $\beta$ at $T_c$ on $\rho(T)$ for specimen B which exhibits a metal-insulator transition, let us consider some $\rho(P)$ isotherms. In Fig. 5 $\rho$ is plotted as a function of P at three temperatures chosen above, near and below $T_c$. The upper axis of Fig. 5 indicates estimated values of $\delta V = \{V(0)-V(P)}/V(0)$ which were obtained using the bulk modulus of 182 GPa. The electrical resistivity is particularly sensitive to changes in volume near and below $T_c$; at temperatures about 60 K above $T_c$ the sensitivity is much reduced. Note that values of $\delta V$ as small as a few parts in one thousand are sufficient to reduce $\rho$ by 50% or more when $T$ is near or below $T_c$. From these data and the data of Fig. 3 it is clear that a reduction of volume in the presence of ferromagnetism (or strong ferromagnetic fluctuations) can have a dramatic influence of $\rho$.

![Graph](Fig. 5. Electrical resistivity as a function of pressure (lower axis) for specimen B at 170 K (triangles), 200 K, squares, and 250 K. $T_c$)
for this specimen is 192.6 K. The upper axis indicates the change in volume estimated with the bulk modulus of 182 GPa. Solid lines are guides to the eye.

With the volume sensitivity of \( \rho \) in mind, let us assess the temperature dependence of \( \delta V_T \) illustrated in Fig. 4. In the temperature region immediately below \( T_c \) where the majority of the decrease in \( \rho \) occurs (i.e. \( T_c < T < T_c-100 \) K) provides a value for \( \delta V_T(T_c) - \delta V_T(T_c-100 \) K) \( \approx 2.5 \times 10^{-3} \). Multiplication of this value by \( B_M \) yields a pressure of 0.45 GPa. We call this the self pressure to indicate that it is the "pressure" generated by the volume change associated with the paramagnetic to ferromagnetic transition. Note that the data in Fig. 5 indicate that a pressure of 0.45 GPa, if it were exerted on the specimen at 200 K (i.e. above \( T_c \)), is large enough to depress \( \rho \) significantly.

Similar considerations for specimen A provide \( \delta V_T(T_c) - \delta V_T(T_c-100 \) K) \( \approx 1.3 \times 10^{-3} \). Multiplication of this value by \( B_M \) yields a self pressure of 0.24 GPa. Consideration of the \( \rho(T) \) curves in Fig. 3 illustrate that a pressure of this magnitude is not sufficient to induce a metal-insulator transition. A report of \( \delta V_T \) data similar to those of specimen A were presented for a ferromagnetic La_{0.88}Ca_{0.12}MnO_3 specimen which did not exhibit a metal-insulator transition [31].

The above arguments highlight volume as a parameter important in understanding the occurrence of a metal-insulator transition in CMR materials. It is by virtue of the extreme sensitivity of the electrical resistivity to changes in volume, that consideration of self pressure becomes relevant. In normal metals, the sensitivity of the electrical resistivity is small in this pressure regime, thereby making any consideration of self pressure irrelevant. On the other hand, this is not the case for all metals. INVAR alloys are an example where the absence of a volume contraction below \( T_c \) results in a positive contribution to \( \rho \) [32]. High temperature superconductors are another example where \( \rho \) is sensitive to pressure. In this case, the temperature-dependent volume results in a sizable contribution to \( \rho \) which adds curvature to the \( \rho(T) \) curve [33].

In Fig. 6 below, we show an additional example of the influence of self pressure on the electrical resistance of CMR materials. This specimen is a single crystal of La_{0.85}Sr_{0.15}MnO_3. This composition is known to exhibit an orthorhombic to rhombohedral phase transition near 300 K [34] whereby the low-temperature phase has a larger volume. All measurements in Fig. 6 were done along the rhombohedral 110 crystallographic direction. The solid curve displays the change in specimen length as a function of temperature and the data points are \( \rho(T) \) normalized to the value at 330 K. In the inset, the temperature dependence of the magnetization in a magnetic field of 4000 Oe; clearly this specimen is ferromagnetic with \( T_c \) near 275 K. Above \( T_c \) there is a discontinuous jump in the length of the specimen as illustrated by the solid line in the figure. This is a first-order phase transition which results in an expansion of the length by an amount \( \Delta l/l = 1 \times 10^{-3} \) as the specimen is cooled. The normalized volume \( \delta V_T \) of this specimen (not shown) expands by \( 1 \times 10^{-3} \) as the specimen is cooled through the transition; this is about a factor of 2 smaller than the expansion reported by Asamitsu et al. [34]. The structural transition is nearly 25 K above the ferromagnetic transition temperature. At a coincident temperature, a discontinuous increase in the electrical resistivity occurs as illustrated by the data points in the figure. It is well-known that \( \rho \) for this particular composition is highly sensitive to applied pressure [35]. We can estimate the self pressure which the specimen experiences by virtue of volume expansion at 300 K. A compressibility of 177 GPa [29] indicates that this expansion corresponds to a negative pressure of 0.18 GPa. There are two items of interest with regard to these data. As the specimen is cooled from room temperature, we see first a volume expansion that is not related to the
ferromagnetic transition. This results in an increase in $\rho$. About 25 K below this structural transition, ferromagnetism sets in with a rapid reduction in volume due to the second-order paramagnetic to ferromagnetic phase transition. This results in a positive self pressure and a reduction in $\rho$ similar to what is observed in specimen B above. Thus, through this example we see that both negative and positive self pressures can result in an increase and decrease in $\rho$, respectively. The electrical resistivity of this specimen is isotropic, so we believe that the change in volume, and not a uniaxial length change, is responsible for the feature in $\rho(T)$ at 300 K. Further measurements on this specimen will be discussed in detail in a forthcoming publication [36].

Fig. 6. Specimen length (solid curve) and normalized electrical resistivity (squares) plotted versus temperature. The magnetization at 4000 Oe as a function of temperature is plotted in the inset.

**IMPORTANCE OF ELECTRON-PHONON COUPLING**

To develop an understanding for the surprising contrast between specimens A and B, one must consider the influence of pressure and composition on the electron-phonon (e-p) coupling. The influence of pressure on the e-p coupling is discussed first. It is clear from the oxygen isotope experiments that an e-p interaction exists in these materials [19] and that it is important for the occurrence of ferromagnetism. Furthermore, Laukhin et al. [20] have recently argued that the strong pressure effect on $\rho$ and $T_c$, particularly in the region of doping where specimens A and B exist, is largely a result of a pressure-induced reduction of the e-p interaction. Other experiments have also suggested the important role of e-p coupling [38]. Millis, Shraiman and Mueller [18] presented a model for the CMR manganites which considered the e-p coupling parameter $\lambda$. In this model, the strong e-p interaction is turned off as $T$ is reduced below $T_c$ and it is also influenced by the level of doping. Consideration of the results for specimen A, it is clear that the occurrence of ferromagnetism alone is not sufficient to result in a metal-insulator transition. When comparison is made between A and B, it becomes apparent that the temperature-dependence of the volume plays an important role in the occurrence of a metal-insulator transition. It is also important here to mention that when pressure is applied to a specimen which exhibits a metal-insulator transition, it decreases the large peak in $\beta(T)$ [37].
illustrates that as the volume and e-p coupling are decreased through hydrostatic pressure, the M-I transition moves to higher temperatures (and metallicity becomes stabilized). Thus, the large peak in \( \beta(T) \) would be greatly reduced if one could reach pressures high enough to create metallicity at all temperatures.

As to the physical basis for the surprising difference in \( \Delta V_T \) between specimens A and B. We suspect that the phase diagram in Ref. 18 provides a clue. The ambient pressure volume of A and B differs by about 0.25% and a reduction of the volume in A (through hydrostatic pressure) results in a M-I transition at \( T_c \). The volume of A is presumably such that its e-p coupling is simply too large to be overcome by the reduction in volume which occurs as \( T \) is reduced to 4 K. These two specimens apparently straddle the FMI/FMM phase boundary in the phase diagram.

CONCLUSIONS

We have argued that the sensitivity of \( \rho \) to hydrostatic pressure (a reduction of volume) is a crucial component in understanding the origin of the metal-insulator transition in CMR materials. We have illustrated this with three ferromagnetic specimens which have various \( \rho(T) \) and \( \Delta V_T \) behaviors. It is argued that the changes in volume which occur at a structural or magnetic transition are large enough to produce self pressures in the range of 0.18 to 0.45 GPa. These self pressures are responsible for large features in the electrical resistivity and are an important component for occurrence the metallicity below \( T_c \). Presumably, this arises because of a strong volume dependence of electron phonon coupling in these particular manganese oxide perovskites. The influence of self pressure on the magnetoresistance was not discussed in this work, and will be discussed elsewhere. Near and below \( T_c \) approximately 50% of the magnetoresistance can be attributed to the magnetovolume [39].

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