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Substantial pressure effects on the electrical resistivity and ferromagnetic transition temperature of $La_{1-x}Ca_xMnO_3$

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The influence of hydrostatic pressure on the electrical resistivity ρ and ferromagnetic transition temperature T_c of $La_{1-x}Ca_xMnO_3$ is presented for $x = 0.21$, 0.33, and 0.40. Pressure strongly decreases ρ and drives T_c up at rates as large as +37 K/GPa for the $x = 0.21$ specimen; this is significantly larger than dT_c/dP values observed in conventional ferromagnets and about eight times larger than dT_N/dP observed in $Ca_{1-x}Sr_xMnO_3$ antiferromagnets. The transport mechanism in these oxides is influenced in a qualitatively similar way by both pressure and magnetic field. The results are interpreted in the framework of the double-exchange interaction involving conduction via magnetic polarons.

The physical properties of the perovskite-based $La_{1-x}(Ca, Sr, \text{ or } Ba)_xMnO_3$ compounds have fascinated scientists for over 40 years. Early work by Jonker and van Santen[1] revealed ferromagnetism over an appreciable concentration range. At the time, it was thought to be the first observation of positive indirect magnetic exchange (i.e., positive superexchange interaction). The exchange was believed to originate within the Mn^{3+}-O-Mn^{4+} complex. Electrical resistance measurements[2] showed activated behavior above the ferromagnetic transition T_c followed by the onset of a transition to metallic behavior at T_c. These observations led Zener to postulate the double-exchange (DE) model, which differs from superexchange or direct exchange, and describes the influence of magnetism on the electrical resistivity.[3] In this model, the conduction electrons mediate the positive magnetic exchange between the next-nearest neighbor manganese ions. The structure of the $La_{1-x}Ca_xMnO_3$ magnetic lattice was investigated by neutron diffraction and numerous antiferromagnetic lattices in the ranges $0 \leqslant x < 0.2$ and $0.45 < x < 1$, and ferromagnetism in the range $0.2 < x < 0.45$ (Ref. 4) were reported. These observations inspired de Gennes[5] to extend the DE model to describe the magnetic lattices.

Surprisingly, it was not until 1989 that magnetoresistance measurements were reported on $Nd_{0.5}Pb_{0.5}MnO_3$.[6] A sharp peak occurred in the electrical resistivity ρ centered at the Curie temperature $T_c = 185$ K with magnetoresistance (MR) $= \{\rho(0) - \rho(20T)\}/\rho(0) \approx 90\%$ near T_c. Measurements were later reported[7] on thin films of $La_{0.72}Ca_{0.25}MnO_3$ with MR $= -53\%$ at 1 T and 210 K. Thin films of $La_{2/3}Ba_{1/3}MnO_3$ were also synthesized[8] and MR values larger than those of Cu/Co multilayers[9] were reported. Subsequently, numerous groups have synthesized thin films with various divalent cation dopants obtaining similar results.[10–12]

Presently it is not clear what physical mechanism is responsible for the large MR effect. Although the DE mechanism may in part be responsible,[7,8] various authors have suggested the importance of magnetic polarons.[6,8,12] Recent considerations indicated that the DE model alone cannot explain the large MR effect[13] and that polaronic effects associated with Jahn-Teller splitting of the Mn *d* states could be an important factor. Detailed measurements have shown that ρ, near *and* below T_c, is related to the bulk magnetization M through the phenomenological relation $\rho \propto \exp\{-M(H,T)/M_0\}$, where M_0 is a constant;[12] these results were interpreted as a signature of magnetic polarons which evolve from small polarons above T_c to large polarons below T_c.

In this report, the electrical resistivity under hydrostatic pressure and the pressure dependence of T_c for some ferromagnetic $La_{1-x}Ca_xMnO_3$ specimens are investigated in order to enhance our knowledge of these important materials. Pressure is a fundamental thermodynamic variable which facilitates a controlled volume change of the physical system; it can influence the electrical conducting properties as well as the interaction responsible for ferromagnetism. Pressure is shown to have substantial effects on the electrical conduction process and T_c in the $La_{1-x}Ca_xMnO_3$ compounds.

Specimens of $La_{1-x}Ca_xMnO_3$ were synthesized by standard solid-state reaction. Stoichiometric amounts of high-purity ($\geqslant 99.99\%$) La_2O_3, $CaCO_3$, and MnO_2 powders were mixed with a mortar and pestle for 5 min. The resulting powder was placed in an Al_2O_3 crucible and reacted at 1050 °C for 20 h. The powder was then reground for 5 min and reacted at 1300 °C for 20 h. This step was repeated two additional times before the final regrinding, pressing into pellets, and firing at 1350 °C. All specimens were slow-cooled in air over a period of 20 h. Relatively hard sintered pellets were obtained and x-ray diffraction showed single-phase perovskite material. Magnetoresistance (MR) measurements, which will be reported in detail later,[14] illustrate MR effects at 5 T for $x = 0.21$, 0.33, and 0.40 as large as −92, −63, and −71 %, respectively. The ferromagnetic transition occurs at 203.3, 267.2, and 271.3 K for the $x = 0.21$, 0.33, and 0.40 specimens, respectively.

Electrical resistivity was measured using a four-wire ac bridge operating at 16 Hz and ac magnetic susceptibility was measured at 85 Hz with a pick-up coil containing the sample which was mounted inside of an excitation coil. Pressure was applied hydrostatically with a standard piston-clamp pressure cell which is described in detail elsewhere.[15] Temperature was determined with a calibrated carbon-glass thermometer.

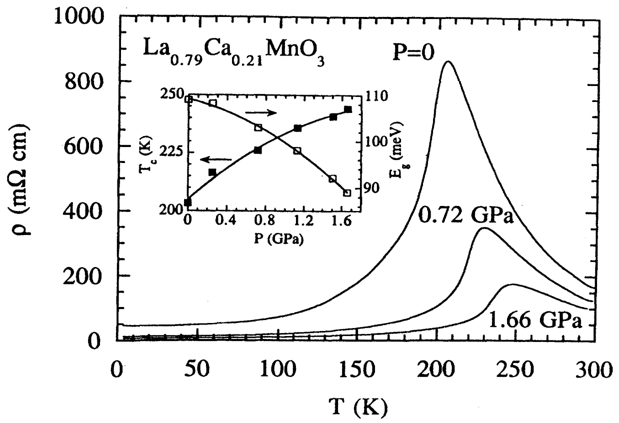

FIG. 1. Electrical resistivity versus temperature at three hydrostatic pressures for $La_{0.79}Ca_{0.21}MnO_3$. In the inset the pressure dependence of T_c (left abscissa) and the pressure dependence of the activation energy E_g (right abscissa) are plotted versus pressure.

For all specimens the temperature dependence of the electrical resistivity at zero pressure was reproduced after releasing pressure.

In Fig. 1 the electrical resistivity ρ versus temperature is plotted at three pressures for a specimen of $La_{0.79}Ca_{0.21}MnO_3$. At zero pressure, the peak in ρ corresponds to the ferromagnetic transition temperature and occurs at $T_c = 203.3$ K; the onset of ferromagnetic order induces a strong drop in ρ. Above T_c, ρ is activated [plots of ln(ρ) vs 1/T and the formula $\rho \sim \exp\{E_g/\mathrm{kT}\}$ were used to determine the activation energy E_g] with an activation energy for charge-carrier hopping of $E_g \approx 108.9$ meV. Pressure strongly reduces ρ near room temperature at a rate of $\sim -45\%$/GPa (-80.4 mΩ cm/GPa) (Ref. 16) and moves T_c to higher temperatures. The inset of Fig. 1 shows T_c (left abscissa) and E_g (right abscissa) versus pressure P. E_g is observed to be weakly dependent on P; an initial slope of $dE_g/dP \approx -5.3$ meV/GPa (or -4.9%/GPa) was observed. On the other hand, T_c is observed to be strongly pressure dependent with a slope near $P=0$ of $dT_c/dP = +36.7$ K/GPa.[16]

In Fig. 2 the electrical resistivity at a number of pressures is displayed for the $La_{0.67}Ca_{0.33}MnO_3$ specimen. Increasing pressure decreases the electrical resistivity near room temperature at a rate of -49%/GPa (-16.5 mΩ cm/GPa) (Ref. 16) and moves T_c to higher temperatures. In an early stage of our investigations, some as-deposited thin-film specimens[12] exhibited a lack of correlation between T_c measured by magnetic susceptibility and that inferrred from the peak in electrical resistivity. As a means of probing this correlation, or lack thereof, we studied the dependence of T_c on pressure for T_c obtained from ac magnetic susceptibility measurements χ_{ac} *and* electrical resistivity for the $x=0.33$ specimen. In the inset of Fig. 2 T_c versus P is plotted, the open symbols are for T_c determined from χ_{ac} while the closed symbols are for T_c determined from $\rho(T)$. Excellent agreement is observed between these two data sets illustrating that the sharp drop in electrical resistivity coincides with the magnetic transition in the entire pressure range. The slope dT_c/dP near $P=0$ is $+15.7$ K/GPa.[16]

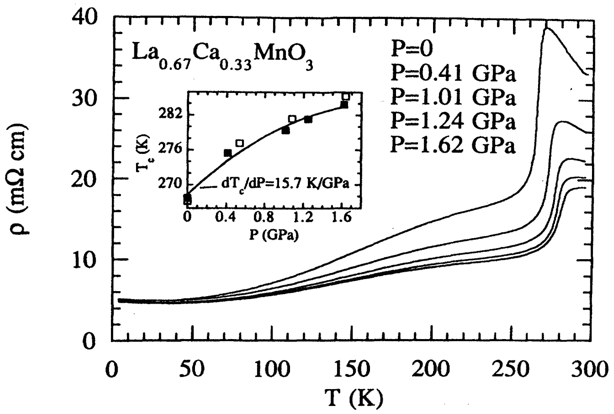

FIG. 2. Electrical resistivity versus temperature at a series of hydrostatic pressures for $La_{0.67}Ca_{0.33}MnO_3$. In the inset the pressure dependence of the ferromagnetic transition temperature T_c, determined by ac magnetic susceptibility (open symbols), and electrical resistivity (filled symbols) are displayed.

Figure 3(a) displays $\rho(T)$ at a number of pressures for a specimen of $La_{0.60}Ca_{0.40}MnO_3$. Pressure drives T_c to higher temperatures at a rate near $P=0$ of $dT_c/dP = +16.0$ K/GPa.[16] The T_c versus P data for $La_{0.60}Ca_{0.40}MnO_3$ are shown in Fig. 3(b); T_c nearly saturates at $P \approx 1.7$ GPa. The electrical resistivity near room temperature is reduced with P at a rate of -55%/GPa (-16.5 mΩ cm/GPa);[16] the increase of ρ near T_c at $P=1.73$ GPa is probably due to specimen cracking since after releasing pressure the temperature dependence of the $P=0$ curve was reproduced, but ρ was larger than the initial value. The electrical resistivity behaves differently for this concentration at temperatures below 200 K. Namely, the $\rho(T)$ curve develops a bump near 120 K

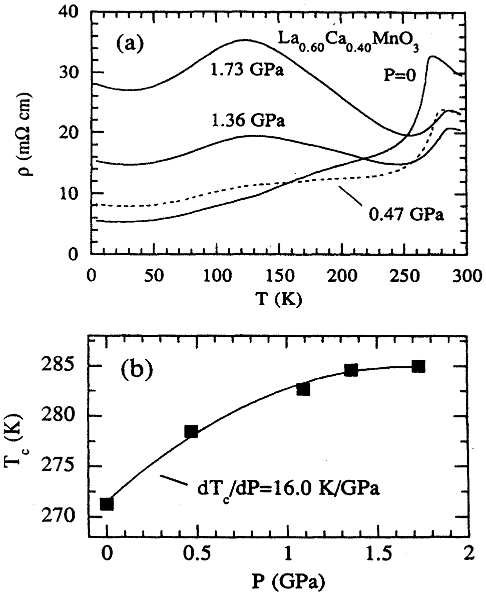

FIG. 3. (a) Electrical resistivity versus temperature at a number of hydrostatic pressures for $La_{0.60}Ca_{0.40}MnO_3$. (b) T_c versus pressure for the $La_{0.60}Ca_{0.40}MnO_3$ specimen.

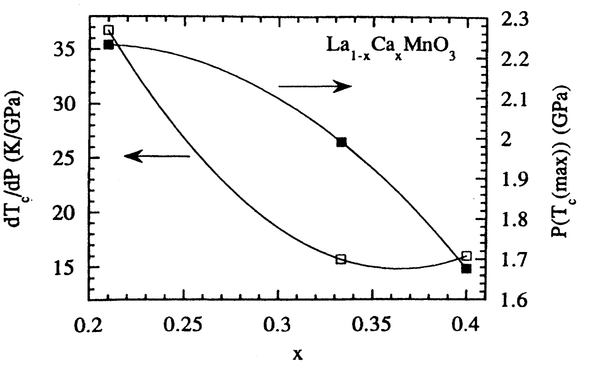

FIG. 4. The pressure derivative of T_c (left abscissa) and the *estimated* pressure where T_c reaches its maximum (right abscissa) versus calcium concentration x.

which is strongly enhanced by pressure. This feature may indicate a magnetic transition from the ferromagnetic state to a canted ferromagnetic state which would decrease electrical conduction within the DE description. Such behavior might arise in the $x=0.40$ specimen, and not in the $x=0.21$ and 0.33 specimens, since it is close to the boundary of the antiferromagnetic state which occurs at $x=0.49$ (Ref. 17) and pressure appears to have a similar effect on ρ and T_c as increasing Ca^{2+} doping (this will be discussed further below). Neutron-diffraction studies at high pressure could address such pressure-induced magnetic ordering.

T_c versus P for all specimens studied herein is not linear and appears to approach a maximum. This is most clearly visible in the $T_c(P)$ data for the $x=0.4$ specimen show in Fig. 3(b). Measurements to pressures above the limitations of our experimental apparatus would be useful to investigate if $T_c(P)$ does indeed develop a negative slope at pressures above 1.8 GPa. An estimate of the pressure $P(T_c(\max))$ where T_c may reach its maximum can be obtained by fitting the T_c versus P data with second-order polynomials; the values $P(T_c(\max))=2.2$, 2.0, and 1.7 GPa for the $x=0.21$, 0.33, and 0.40 specimens, respectively are obtained. In Fig. 4 the dT_c/dP (left abscissa) versus x data and the $P(T_c(\max))$ (right abscissa) versus x data are shown; these data will be discussed below.

An interesting feature of the data (neglecting the unusual behavior of the $x=0.40$ specimen below 250 K) is that the influence of pressure on ρ qualitatively resembles the influence of magnetic field on ρ (at zero pressure).[6–8,10–12] In addition, measurements of $\rho(T,H)$ by Khazeni *et al.*[18] on Pb-doped single crystals of $La(Pb)MnO_3$ indicate that pressure also reduces the Mr effect. Thus the decrease of ρ under application of pressure not only mimics the effect of magnetic field, it also destroys the anomalously large magnetoresistance of this system. Apparently, a reduction in volume erodes the unusual physical state which is responsible for the anomalously large magnetoresistance. These observations establish the importance of changes in volume (i.e, pressure) for not only electrical transport, but magnetotransport as well.

According to the DE model, transfer of charge carriers from site to site mediates the ferromagnetic exchange.[3,5] The transfer integral for electrical conduction between neighboring Mn sites is approximated by $t_{\mathrm{eff}}=t_0 \cos\{\Theta/2\}$; when the angle Θ between two neighboring spins is zero (i.e., ferromagnetic alignment) t_{eff} is maximized. It follows from this model that the dramatic decrease of ρ with decreasing temperature near T_c (i.e., as Θ goes to zero) *at zero pressure* occurs as a result of broadening of the bandwidth, which is proportional to t_{eff}, resulting in an increase of charge-carrier mobility. Pressure would be expected to increase t_0, whereas H and T would affect the degree of magnetic order and in turn the $\cos\{\Theta/2\}$ term.

The sensitivity of the electrical resistivity to pressure near T_c is particularly strong. This is in part due to the pressure-induced rapid movement of T_c toward higher temperatures, but it is mainly a result of particular sensitivity of ρ in the neighborhood of T_c to pressure. This is seen most clearly in the $x=0.21$ specimen where the activation energy and ρ decrease with pressure. As mentioned above, pressure and magnetic field have similar effects on ρ through their respective influences on t_{eff}. The resistivity above T_c can be considered as arising from the propagation of magnetic polarons,[6,8,12,13] which move via thermally activated hopping. The bandwidth for a polaron is given by $J_B \sim \exp(-\alpha R)$ where α is a constant and R is the distance between two neighboring polarons.[19] Pressure decreases R and has a strong positive effect on J_B (due to its exponential dependence on R) thereby increasing the charge-carrier mobility and decreasing ρ. The pressure-induced increase of charge-carrier mobility would increase t_0 and be partly responsible for enhancing the DE ferromagnetic coupling strength which increases T_c.

In Fig. 4 dT_c/dP is observed to drop off strongly with increasing x and pass through an apparent minimum while $P(T_c(\max))$ moves to lower pressures with increasing x suggesting the development of a peak in T_c versus P at high x. The largest dT_c/dP and $d\rho/dP$ values occur for the specimen with the highest electrical resistivity (and lowest value of x). These observations indicate that the pressure dependence of T_c is a strong function of the doping level and are reminiscent of effects observed in high-temperature superconductors[20] where the total charge-carrier concentration n increases with pressure. In the present work a limited number of dT_c/dP versus x data points and a lack of experimental information about $n(P)$, precludes a reasonable analysis in this regard; future investigations should address this aspect. At this stage it appears reasonable that $n(P)$ could be nonzero, this would also enhance the ferromagnetic DE coupling and decrease ρ.

The observed values of dT_c/dP are larger than those for other ferromagnetic materials such as $SrRuO_3$ (also a perovskite with $dT_c/dP \approx -5.7$ K/GPa),[21] Ni ($dT_c/dP=+3.2$ K/GPa), Fe ($dT_c/dP=0$), Co ($dT_c/dP=0$),[22] Sc_3In ($dT_c/dP=+1.7$ K/GPa),[23] but comparable to that observed for ferrimagnets such as $Y_3Fe_5O_{12}$ ($dT_c/dP=+12.5$ K/GPa).[22] Experiments on $Ca_{1-x}Sr_xMnO_3$ (Ref. 24) showed that the pressure dependence of the Néel temperature were in the range $dT_N/dP \sim +4$ K/GPa; this is five to ten times weaker than in the ferromagnetic specimens investigated herein. In this case the ferromagnetic double-exchange interaction is presumably more highly pressure dependent than direct (or super-) exchange (assumed responsible for the antiferromagnetism) in similar compounds because, in addition to the normal effects of pressure, double exchange depends directly on the charge-carrier mobility and number of total charge carriers which in this system increase with P. In addition, large values of dT_c/dP suggest that strong magnetovolume effects will be observed in these materials.

An interesting observation is that the larger A = Sr and Ba ions, when substituted for Ca in $La_{1-x}A_xMnO_3$ possess higher values of T_c. This is contrary to chemical pressure considerations which would argue that, since dT_c/dP is strongly positive for the A = Ca specimens, a larger A ion should result in a *lower* T_c. This discrepancy was discussed in early studies on $Ca_{1-x}Sr_xMnO_3$ (Refs. 24 and 25) as arising from the fact that Ca is more covalent than Sr and hence Ca competes with the Mn-O-Mn interaction; such covalency could be expected to make dT_c/dP less positive. In such a framework, $La_{1-x}Sr_xMnO_3$ would have larger positive values of dT_c/dP than A = Ca specimens. Early χ_{ac} studies on ferromagnetic $La_{0.75}Sr_{0.25}MnO_3$ show[26] that $dT_c/dP = +6$ K/GPa, which is smaller than the values observed herein. Perhaps the more important factor in determining T_c is the Mn-O-Mn bond angle, which systematically varies with the A-ion size, and was recently observed to reduce the magnetic exchange and electron hopping as the angle decreased from 180°.[27] Future structural investigations under pressure could address the exact influence of P on the $La_{1-x}Ca_xMnO_3$ crystal structure.

In summary, values of dT_c/dP in $La_{1-x}Ca_xMnO_3$ are significantly larger than in conventional ferromagnets, and about eight times stronger than dT_N/dP in $Ca_{1-x}Sr_xMnO_3$. The electrical resistivity is also strongly reduced by the application of pressure and dT_c/dP is a strong function of x indicating that pressure increases charge-carrier mobility and total charge-carrier concentration which in turn enhance the ferromagnetic double-exchange interaction and T_c. This work establishes pressure as an important variable for large MR perovskites.

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