Effect of Pressure on the Magnetoresistance of Single Crystal $Nd_{0.5}Sr_{0.36}Pb_{0.14}MnO_{3-\delta}$

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To investigate the observed huge variations in magnetoresistance between different samples of manganite perovskites we have performed the first high-pressure measurement of magnetoresistance in single crystal $Nd_{0.5}Sr_{0.36}Pb_{0.14}MnO_{3-\delta}$. Both resistivity and magnetoresistance are strongly suppressed upon application of pressure. The decrease in magnetoresistance with increasing pressure rules out substrate-induced compressive strain as a source of enhanced magnetoresistance. Instead, the magnetoresistance differences between samples are ascribed primarily to the more abrupt nature of the semiconductorlike to metallic phase transition at lower temperatures.

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The discovery of anomalously high negative magnetoresistance (MR) in perovskite-structured manganites has prompted considerable theoretical and experimental interest [1–3]. The motivation for this interest is twofold: First, there are numerous potential sensor applications for high-temperature, high MR materials. Second, the detailed mechanism for the drop in resistivity upon application of magnetic field is not yet understood. One major outstanding puzzle is the more than thousandfold difference in the magnitude of peak MR between samples. Explanations for this variation include epitaxy-induced strain in thin films and the shorting out of magnetoresistive regions by nonmagnetoresistive grain boundaries in polycrystalline samples [1]. Clarification of this issue should be a crucial step towards the eventual understanding of the MR mechanism. We have measured the pressure dependence of the magnetoresistance for single crystal $Nd_{0.5}Sr_{0.36}Pb_{0.14}MnO_{3-\delta}$, a measurement ideally suited to clarifying the role of both grain boundaries and stress in the MR mechanism.

An external pressure of 10.7 kbar is found to raise the resistive transition temperature of single crystal $Nd_{0.5}Sr_{0.36}Pb_{0.14}MnO_{3-\delta}$ by 20 K. The peak MR is reduced by ~50%, a result in conflict with the notion that an epitaxially induced lattice compression induces the increased peak MR observed in some thin-film samples. Although lack of grain boundaries in high quality thin films has been suggested as a reason for the increased peak MR in these films, the moderate size of the peak MR in our single crystals indicates that a lack of grain boundaries is not the crucial ingredient for achieving the largest peak MR. Instead, the results suggest that increased peak MR is a generic consequence of a lower transition temperature from a high-temperature semiconductorlike phase to a low-temperature metallic phase. The effects of externally applied hydrostatic pressure can be interpreted in terms of a pressure-induced increase in electronic hopping amplitude.

The perovskite manganites are of general form $A_{1-x}B_xMnO_3$, where A and B denote 3+ and 2+ ions such as Pr^{3+} and Sr^{2+}. The (A,B) ions are located at the corners of a simple cubic unit cell, the Mn ions are at the center of the cube, and the oxygen ions are at the center of each face of the cube [4]. In 1989 very high peak MR was reported on single crystals of $Nd_{0.5}Pb_{0.5}MnO_{3-\delta}$ by Kusters *et al.* [2]. More recent work [1] has demonstrated an even larger peak MR for thin film specimens of the related material $La_{0.67}Ca_{0.33}MnO_{3-\delta}$. In general, the $A_{1-x}B_xMnO_3$ materials appropriately doped with 2+ valence B species undergo a semiconductorlike to metallic phase transition upon cooling. The transition is associated with a sharp peak in the electrical resistivity. Magnetization studies show that this peak resistivity temperature T_{PR} is very close to the magnetic Curie temperature T_C [5,6]. A peak in the negative MR also occurs very close to T_C. The magnitude of the negative peak in MR varies greatly between samples, with certain $La_{1-x}Ca_xMnO_3$ thin films [1] and Y-doped polycrystalline samples [7] showing MR peaks hundreds or thousands of times larger than those of polycrystalline $La_{1-x}Ca_xMnO_{3-\delta}$ [4] or $(Nd_{1-y}Pr_y)_{0.67}Sr_{0.33}MnO_{3-\delta}$ [8]. One possibility is that lattice compression induced by either epitaxial growth (the lattice constant of $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ is 3.84 Å versus 3.79 Å for the $LaAlO_3$ substrate of Ref. [1]) or the introduction of smaller radius Y for La [7] somehow causes the increased peak MR observed in these samples. The measurement of the pressure dependence of the resistivity and MR would provide a direct test of the influence of the lattice constant upon the magnitude of MR in the manganite perovskites.

Single crystals of $Nd_{0.5}Sr_{0.36}Pb_{0.14}MnO_{3-\delta}$ were grown using a flux method described in detail elsewhere [6]. Specimens were typically near-perfect cubes 1 mm on a side with shiny faces. The crystals were characterized by x-ray measurements [6] yielding a cubic structure with lattice constant 3.86 Å. dc magnetization measurements on one sample confirmed the close relationship between the magnetic and resistive transitions [6]. The cation and Mn stoichiometries were determined with energy dispersive

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x-ray spectroscopy (EDX). In the present study, the dc electrical resistivity was measured using a conventional four-probe configuration. The magnetoresistance was measured in a superconducting solenoid at 7 T. After both resistance and magnetoresistance were measured at zero pressure, the sample was transferred to a self-clamping pressure cell where roughly a 12 kbar of hydrostatic pressure was locked in at room temperature. Fluorinert FC-75 was used as the pressure medium. Both resistance and magnetoresistance were again measured for the same sample under pressure. The pressure inside the cell was continuously monitored using a calibrated manganin coil. Because of differences in thermal expansion coefficients between the pressure medium and the pressure cell, the pressure inside the cell decreased as the temperature was lowered, from 12 kbar at 300 K to 9 kbar at 4.2 K.

Figure 1 shows the normalized resistivity ρ of a crystal of $\mathrm{Nd_{0.5}Sr_{0.36}Pb_{0.14}MnO_{3-\delta}}$ measured at zero and high pressure, with and without an applied magnetic field. The zero pressure, zero field resistivity peak at $T_{\mathrm{PR}} \approx 204$ K identifies the semiconducting to metallic phase transition temperature and the Curie temperature T_C. The temperature coefficient of resistivity changes from negative to positive upon cooling through T_{PR}. At an applied pressure of 10.7 kbar T_{PR} is increased to $\approx$225 K, again with zero applied field. This yields $\Delta T_C/\Delta P = 2.0$ K/kbar averaged over the pressure range. The value of the peak resistivity is depressed by 53% with application of 10.7 kbar of pressure. The residual resistivity also changes by 42% at $\approx$9.5 kbar.

Figure 1 also shows resistivity data for an applied field of 7 T. Under zero pressure, the applied magnetic field dramatically reduces the peak resistance and shifts the transition temperature upward, consistent with previous observations on related materials [2,5,6,8]. Under high pressure, an applied field has a similar effect: The (pressure reduced) resistance peak is further depressed by application of the field, and T_{PR} is shifted to a yet higher temperature. In a sense, magnetic field and pressure seem to have similar effects near the transition: They both depress the resistance peak and shift T_{PR} to higher temperature. For zero field, $\Delta T_{\mathrm{PR}}/\Delta P = 2.0$ K/kbar, while for zero pressure, $\Delta T_{\mathrm{PR}}/\Delta H = 6.9$ K/T. Although both pressure and magnetic field push T_{PR} to higher temperature and reduce the peak resistivity, there is a subtle distinction between the two external perturbations in that under application of magnetic field the semiconducting to metallic phase transition is rather broad and diffuse, whereas the same transition is much sharper and abrupt when only pressure is applied.

Figure 2 shows the MR of $\mathrm{Nd_{0.5}Sr_{0.36}Pb_{0.14}MnO_{3-\delta}}$ with and without an average applied pressure of about 10 kbar. We here define magnetoresistance as

$$\mathrm{MR} = \frac{|R(P,T,H = 7\ \mathrm{T}) - R(P,T,H = 0)|}{R(P,T,H = 7\ \mathrm{T})}. \tag{1}$$

Application of pressure results in overall reduction in the peak (negative) magnetoresistance from 3.4 at zero pressure to 2.2 at 10.7 kbar. There is a concomitant 20 K upward shift of the MR peak under pressure. By comparing Figs. 1 and 2, it is apparent that the peaks of both the MR and resistivity occur roughly at the same temperature [although we have not measured magnetization of our crystals under pressure to determine $T_C(P)$, we surmise that under pressure T_{PR} also tracks T_C [9]]. A surprising feature of Fig. 2 is that the MR is roughly independent of pressure above $T_{\mathrm{PR}}(P)$. This would imply that the ratio $R(P,T,H = 0)/R(P,T,H = 7\ \mathrm{T})$ is nearly independent of pressure for temperatures larger than $T_{\mathrm{PR}}(P)$. This in turn might suggest for the high-temperature resistivity an interesting functional form

$$R(P,T,H) \approx r(T,H)f(P), \tag{2}$$

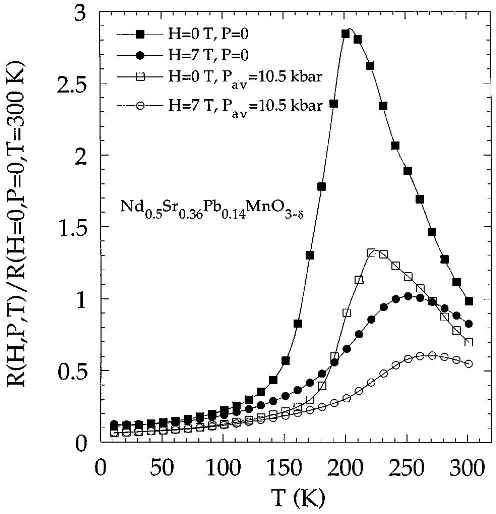

FIG. 1. Temperature dependence of the normalized resistivity for different combinations of applied magnetic field and pressure. Solid lines are guides for the eye.

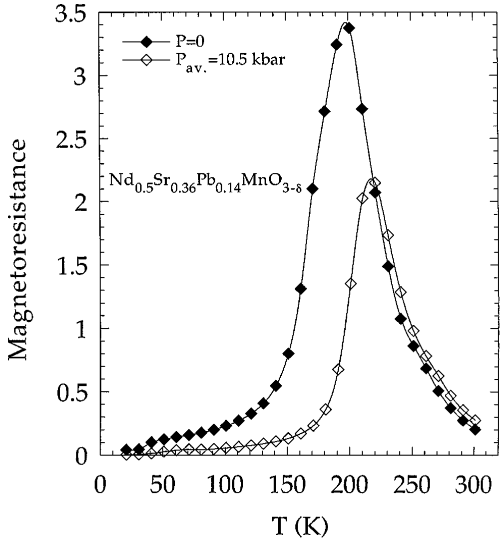

FIG. 2. Magnetoresistance as a function of temperature under pressure and in $P = 0$. Solid lines are guides for the eye.

where $r(T,H)$ is a function of only temperature and magnetic field, and $f(P)$ is a function of only pressure. Further investigation should shed light on the relevance of this provisional factored expression for $R(P,T,H)$.

Application of pressure both increases the temperature and decreases the magnitude of the MR peak. The increase in the transition temperature can be interpreted as a consequence of increased electronic hopping amplitudes as a function of pressure. Within double exchange theory [10–12] hopping of valence electrons is suppressed between atoms of unlike ionic spin. The transition to the low-temperature spin-ordered state is accompanied by a decrease in electronic kinetic energy due to increased delocalization of the electronic wave function over all allowed sites. Increased overlap between adjacent orbitals at high pressure implies a greater role for electronic kinetic energy in determining the stable structure for the system. Within this picture, the application of pressure stabilizes the low-temperature phase and leads to an increase in the transition temperature.

To reiterate, Hund's rule dictates that the site energy of a charge carrier aligned with the underlying ionic spin is lower than that of an antialigned carrier. In the high-temperature spin-disordered phase the set of spin-up carriers predominantly occupies the spin-up ions, while the set of spin-down electrons is mostly restricted to the spin-down ions. Upon spin ordering, the entire set of charge carriers may occupy all of the ionic sites. The carriers gain delocalization energy to the extent that there is overlap between the wave functions of adjacent orbitals. An increase in pressure will increase this overlap and therefore should accentuate the stability of the low-temperature ordered phase. In contrast, the decrease in the Mn-O-Mn bond angle upon introduction of chemical pressure decreases the relevant overlap integrals and consequently decreases T_C [13].

In the particular case of a pressure-induced increase in the transition temperature, we can envision an additional mechanism for a reduction in the peak magnetoresistance. The reduction in slope of resistivity versus temperature under application of pressure is in excess of the fractional reduction in the value of the resistivity itself, indicating that the activation energy is lowered by external pressure. Assuming that conduction in the high-temperature phase proceeds by means of polaronic hopping, the decrease in activation energy can be explained as a reduced local relaxation around the more quickly hopping electrons. The decrease in activation energy leads to a decreased high-temperature resistivity, a less pronounced resistive transition, and therefore a lower peak magnetoresistance. A hopping-induced destabilization of a polaronic phase is also consistent with the observed increase in transition temperature.

The generic decrease in the magnitude of the magnetoresistance peak with increasing transition temperature in perovskite GMR materials can be given a straightforward explanation: The difference in resistivities between a metallic phase and a semiconductorlike phase decreases with increasing temperature, yielding a lower-slope resistive transition for a higher-temperature transition. The same field-induced change in transition temperature yields a smaller change in resistivity the lower the sensitivity of resistance to temperature in the transition region, yielding a smaller peak magnetoresistance for higher transition temperatures. Figure 3 shows a compilation of published results for the peak MR versus T_C for a variety of $A_{1-x}B_x\mathrm{MnO}_{3-\delta}$ materials at fields ranging from 5 to 12 T [2,7,14]. Considering the variations in materials and field strengths, a surprisingly robust inverse relationship between T_C and the peak MR is observed. The maximum magnetoresistance at a given field appears to be a universal function of the transition temperature from the insulating to the metallic phase.

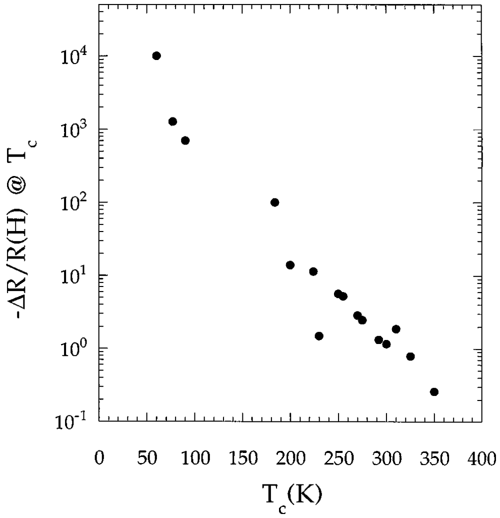

FIG. 3. Compiled maximum MR vs T_C from published data (Refs. [2,7,14]).

The effects of pressure on the magnetoresistance of single crystal $\mathrm{Nd}_{0.5}\mathrm{Sr}_{0.36}\mathrm{Pb}_{0.14}\mathrm{MnO}_{3-\delta}$ have been studied for the first time. An overall drop in resistivity and magnetoresistance is observed under pressure. The peaks in resistivity and MR corresponding to ferromagnetic ordering are moved to a higher temperature by $\sim$20 K/kbar. The pressure-induced increase in transition temperature and decrease in peak MR can be interpreted within double exchange theory, wherein the electronic hopping amplitude increases under pressure. The behavior of MR under pressure follows the generic trend towards lower peak MR for higher transition temperatures, suggesting that the large variations in peak MR in the literature can be ascribed in large part to variations in the transition temperature from the semiconductorlike to the metallic regime.

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Note added.—Recent measurements [15] on polycrystalline specimens of $La_{1-x}Ca_xMnO_3$ show a pressure dependence of zero-field resistivity similar to that described here.

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