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Pr-doping of the High-magnetoresistance Perovskite $Nd_{2/3}Sr_{1/3}MnO_3$

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We have investigated the effect of Pr-doping on the Nd-sites in the high magnetoresistance (MR) perovskite $Nd_{2/3}Sr_{1/3}MnO_3$. For polycrystalline materials, negative MR as high as ~ 235% is observed near 237K in pure $Nd_{2/3}Sr_{1/3}MnO_3$. The substitution of Pr for Nd leads to a reduction in the overall MR, and an increase of the MR-peak temperature. We investigate the possibility that the large negative MR originates from the formation of localized magnetic polarons.

In recent years, metallic multilayers and superlattices such as Fe/Cr[1-3] have been of great interest because of their giant magnetoresistance (GMR) properties. The physics of GMR is intriguing; in addition there exists enormous applications potential for GMR materials.

Although three-dimensional perovskite-type manganese compounds (manganites) were extensively studied in the early 1950's[4-6], it was not until very recently that their extraordinary magnetoresistance (MR) properties were appreciated. The manganites are of the general form $R_{1-x}Me_xMnO_3$ where R stands for La, Y, and rare earths and Me denotes alkali-earth metals. The large R and Me ions are located at the corners of a simple cubic unit cell, the small Mn ion is at the center of the cube, and the oxygen ions are at the face centers of the cube. Examples are $Nd_{1-x}Pb_xMnO_3$[7], $La_{1-x}Ba_xMnO_3$[8], and $La_{1-x}Ca_xMnO_3$[9-10].

Manganites may have advantages over conventional (superlattice) GMR materials for applications purposes. Significantly, under optimized conditions, the MR of the manganites is much larger than that of the conventional GMR materials[7, 9].

The origin of the MR in manganites is presently the subject of much speculation. The materials are typically "semiconducting" at high temperatures (above room temperature) and "metallic" at low temperatures (below ~ 100K); there is a peak in the electrical resistivity in the crossover regime. The MR, defined here as $\Delta R/R_H = [R(H) - R(H=0)]/R(H)$, typically has a peak near the crossover regime. The peak resistivity temperature, peak MR temperature, and the magnitude of the MR all appear to depend sensitively on sample processing conditions (reflecting an apparent dependence on charge doping by variable oxygen concentration).

We have investigated the electrical resistivity and MR behavior in Pr-doped $Nd_{2/3}Sr_{1/3}MnO_3$, i.e. in $(Nd_{1-y}Pr_y)_{2/3}Sr_{1/3}MnO_3$, with y varying in the range of 0 to 1.0. Increasing Pr concentration systematically shifts the "semiconductor-to-metal" transition to higher temperature, with a concomitant shift in the peak MR temperature and an overall depression in the MR magnitude. We use the transport results to investigate possible origins for the anomalous MR.

Bulk polycrystalline specimens of stoichiometric compositions were prepared using a standard solid-state reaction technique [4]. The metallic oxides or carbonates of ≥ 99.9% purity were mixed, ground, and annealed at 1000 °C for 40 hours in a pure oxygen flow environment with one intermediate regrinding. The powder was pressed into pellets after the intermediate regrinding. The sintered pellets were reground, pressed again into pellets, and then fired at 1400 °C for 16 hours in air. Since different heat treatments can alter the Mn^{3+}/Mn^{4+} ratio and result in a dramatic change of the $\Delta R/R_H$ value and the temperature of peak magnetoresistance, all samples presented in this study were as-synthesized and underwent identical heat treatment. This insures similar oxygen content for all specimens.

X-ray diffraction patterns showed that the crystal symmetry of the samples is cubic with lattice constant a = 3.86 Å. No other reflections other than those of the cubic structure were observed. The electrical resistance of the samples was measured using a conventional four-probe technique with temperature varying in the range of 4 K to 350 K and applied magnetic fields of up to 7 T.

Figure 1 shows, for the pure parent compound $Nd_{2/3}Sr_{1/3}MnO_3$, the temperature dependence of the normalized resistance for zero applied field and for H=7T. R_o is defined as R(T=300K, H=0). For H=0, the characteristic "semiconductor-to-metal" transition is observed with a peak or crossover temperature T_{co} near 237K. Below 237K the H=0 resistance falls with decreasing temperature, and between 40K and 210K it is well fit by the functional form $a + bT + cT^3$ with a, b, and c constants. As detailed in the inset of Fig. 1, near 25K there is a shallow minimum in R, reminiscent of Kondo system behavior. The H=7T data of Fig. 1 demonstrate a dramatic negative magnetoresistance in $Nd_{2/3}Sr_{1/3}MnO_3$ over a wide temperature range. Grossly speaking, the effect of the magnetic field is to suppress the peak in the resistance near 237K-- the resistance becomes overall less temperature dependent. At temperatures at and above 350K, virtually no MR is observed. At

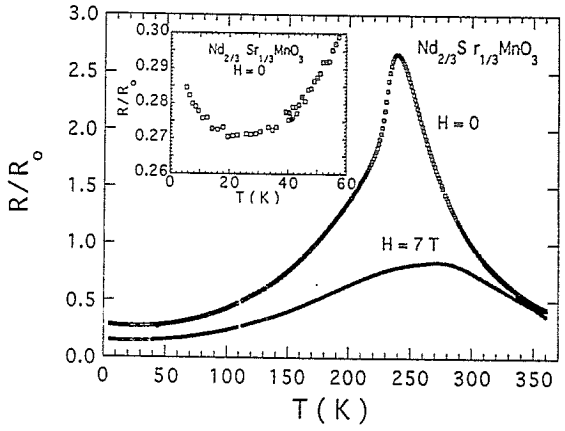

Fig. 1. Temperature dependence of the normalized resistance for zero applied field and for H = 7 T. R_o is defined as R (T=300K, H=0). The inset shows the low temperature behavior of the zero-field resistance data in detail.

temperatures below approximately 100K, the MR is modest and roughly temperature independent. The shallow minimum in R near T=25K persists even in fields to 7T.

Figure 2 shows the effects of Pr doping. Data are shown for three different specimens of $(Nd_{1-y}Pr_y)_{2/3}Sr_{1/3}MnO_3$, with respective Pr doping values of y = 0, 0.3, and 1.0. Figure 2a shows normalized H=0 resistance data. All of the samples show similar resistance behaviors, with a pronounced semiconductor-to-metal transition. With increasing Pr concentration, the resistance peak at T_{co} is reduced in magnitude and T_{co} increases. The high temperature resistance is largely unaffected by Pr doping.

Figure 2b shows the H=7T MR for the same sample set. The MR has a peak at a temperature close to but slightly less than the resistance crossover temperature T_{co}. The temperature of the peak magnetoresistance increases from 237K to 283K and its magnitude decreases from 235% to 94% as the Pr doping increases from y=0 to y=1.0. The decrease in the maximum value of the MR is similar to the behavior of the resistance peak observed in Fig. 2a where the magnitude of the resistance peak is diminished with increasing Pr concentration. Figure 2b also shows that the width of the MR peak is relatively unaffected by Pr doping. In addition, both well above and well below the crossover temperature, the MR becomes roughly independent of Pr concentration.

Figure 3 shows the applied magnetic field dependence of the normalized resistance for a different sample of Pr-doped $Nd_{2/3}Sr_{1/3}MnO_3$ with y=0.3. At $T < T_{co} = 256K$, the resistance decreases rapidly at low fields and then continues to decrease with a much lower rate at high fields. The characteristic field separating these two regimes increases with increasing temperature. The fast fall-off of resistance with increasing field in the low-field regime is significant for some device applications where only low fields are accessible. At T near T_{co}, the normalized resistance shows the largest low-field sensitivity. For $T > T_{co}$, no two distinctive field regimes exist and the decrease of the resistance with increasing field is rather slow

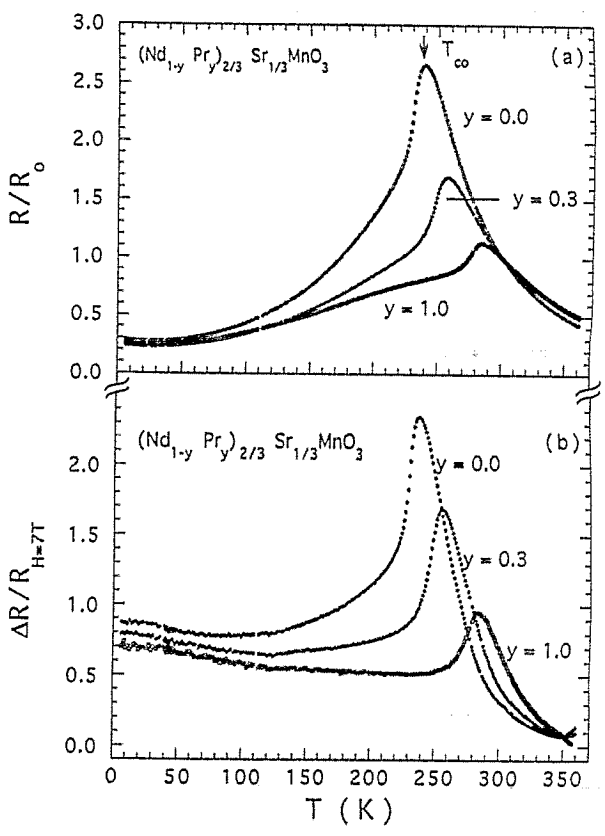

Fig. 2. Temperature dependence of (a) the zero-filed resistance and (b) the magnetoresistance, $\Delta R/R_{H=7T}$ for three samples of $(Nd_{1-y}Pr_y)_{2/3}Sr_{1/3}MnO_3$ with respective Pr doping values of y=0.0, 0.3, and 1.0.

at low fields. In the entire temperature regime measured, the magnetoresistance is not saturated up to H = 7 T.

We now discuss these results. The $RMnO_3$ materials are typically antiferromagnetic insulators [11,12]. The magnetic ordering in $RMnO_3$ consists of ferromagnetic layers of Mn-O that are stacked antiferromagnetically and separated from each other by a R-O layer. The substitution of Me ions on the R sites leads to a mixed Mn^{3+}/Mn^{4+} state. When a high proportion of Mn^{4+} is present, $R_{1-x}Me_xMnO_3$ becomes ferromagnetic and conductive. Ferromagnetic ordering of these manganites has been well accounted for by double-exchange theory[6]. A Sr content of 1/3 in $(Nd_{1-y}Pr_y)_{1-x}Sr_xMnO_3$ samples is then expected to result in ferromagnetic spin ordering transitions. A Curie temperature of 263 K has been observed in $(Nd, Pr)_{0.7}Sr_{0.3}MnO_3$[4].

The origin of the large MR peak observed in the manganites has not been established. The fact that the peak temperature of the large MR is very close to the ferromagnetic ordering temperature and that the peak temperature is strongly field-dependent suggests that a spin-dependent mechanism is responsible for the giant magnetoresistance.

We explore the possibility that the observed resistivity behavior above the resistivity-peak temperature T_{co} may reflect the formation of magnetic polarons [8,13,14]. A magnetic polaron is a conducting electron which

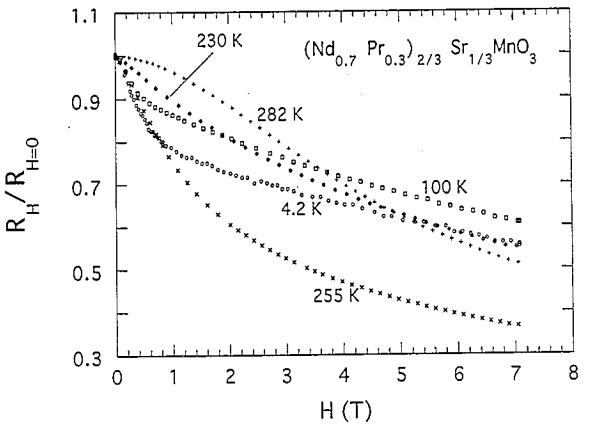

Fig. 3. Magnetic field dependence of the resistance for a typical $(Nd_{1-y}Pr_y)_{2/3}Sr_{1/3}MnO_3$ sample with y = 0.3. The resistance are normalized by their respective zero-field values.

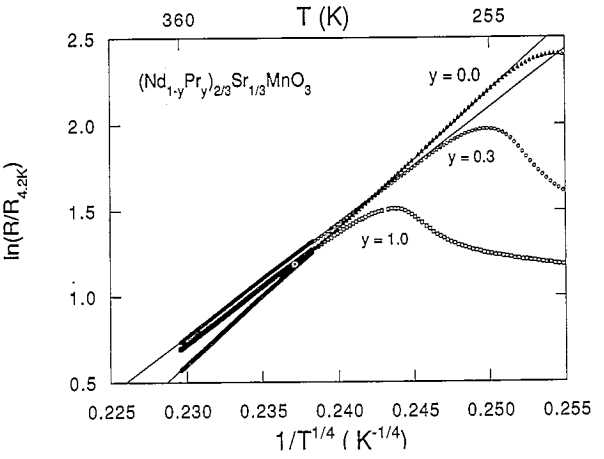

Fig. 4. $\ln(R/R_{4.2K})$ versus $T^{-1/4}$ plot for the $(Nd_{1-y}Pr_y)_{2/3}Sr_{1/3}MnO_3$ samples with y=0.0, 0.3, and 1.0 near and above T_{co}. The lines are linear fits to the data.

polarizes the magnetic moments of the surrounding ions, forming a small ferromagnetic region. Magnetic polarons could become localized as a result of magnetic interaction as was originally suggested by Mott [15]. Conduction by localized magnetic polarons then proceeds via a variable range hopping process. The resistivity in the hopping region should follow Mott's classic $\ln(R/R_0) \sim T^{-1/4}$ law appropriate for a three dimensional system.

Figure 4 shows the zero-field resistance near and above T_{co} in a $\ln(R/R_{4.2K})$ vs. $T^{-1/4}$ plot for three different specimens of $(Nd_{1-y}Pr_y)_{2/3}Sr_{1/3}MnO_3$, with y = 0, 0.3, and 1.0. Linear behavior is observed over a fairly wide temperature range starting just above T_{co}. Fitting the H=0 resistance data in this temperature regime with a $\ln(R/R_{4.2K}) \sim 1/T$ functional form leads to an inferior fit, indicating that a thermally activated mechanism with $R/R_{4.2K} \sim e^{\Delta/KT}$ is not relevant. The $\ln(R/R_{4.2K}) \sim T^{-1/4}$ behavior observed in our resistivity data is consistent with a variable range hopping mechanism of localized magnetic polarons.

Below the resistivity peak temperature T_{co}, the formation of magnetic polarons becomes impossible due to the ferromagnetic ordering of the materials. The collapse of the hopping behavior of the magnetic polarons results in the rapid drop-off of the resistivity. The application of an external field increases the ferromagnetic ordering and suppresses the formation of magnetic polarons, leading to the MR near T_{co} and a shifted broad resistivity peak.

In conclusion, we have studied the magnetoresistance properties of Pr-doped $Nd_{2/3}Sr_{1/3}MnO_3$ manganites. A magnetoresistance as high as 235% is observed in $Nd_{2/3}Sr_{1/3}MnO_3$. The substitution of Pr for Nd reduces the overall MR and shifts the temperature of the peak magnetoresistance to a higher temperature. The resistivity peak may originate from the formation of localized magnetic polarons. The collapse of the hopping behavior of magnetic polarons under an external field would then be the origin of the anomously large negative magnetoresistance in these manganites.

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