

RAPID COMMUNICATION

Spectacular Increase of Resistivity by Thermal Cycling under a Magnetic Field in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.99}\text{Cr}_{0.01}\text{O}_3$

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The resistivity of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.99}\text{Cr}_{0.01}\text{O}_3$ under $H = 4\text{ T}$ shows unusual instability against thermal cycling between 250 and 5 K. The resistivity at 10 K change from $100\ \Omega\text{ cm}$ in the first cycle to more than $10^6\ \Omega\text{ cm}$ in the fifth cycle. However, magnetization decreases only by 1.2% between the first and the fifth cycles. The unusual enhancement of resistivity is suggested to be due to strain-induced localization of charge carriers. © 2001 Academic Press

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Rare earth manganites of the general formula $\text{RE}_{1-x}\text{AE}_x\text{MnO}_3$ (RE and AE are trivalent rare earth and divalent alkaline earth ions, respectively) have been studied vigorously over the past few years because of their extraordinary reduction in resistance under external magnetic fields (1). There appears to be more than one mechanism responsible for colossal magnetoresistance in these compounds. In $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, which is a prototype for the compounds showing paramagnetic insulator–ferromagnetic metal transitions, a large magnetoresistance in the vicinity of Curie temperature appears to be caused by destruction of magneto-elastic polarons (2). The large magnetoresistance of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, which undergoes a metal–metal transition as T is lowered from $T > T_C$ to $T < T_C$ (T_C is the ferromagnetic Curie temperature) can be understood in the framework of reduction in spin-disorder scattering (3). The magnetic-field-driven charge-ordered antiferromagnetic insulator–ferromagnetic metal transition in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ is qualitatively understood in terms of “melting” of charge order in a magnetic field (4). However, the stability of the low-resistive state in a magnetic field is rarely studied. Anane *et al.* (5) reported that the magnetic-field-driven low-resistive state of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ is unstable after removal of the magnetic field. They find that isothermal resistivity abruptly jumps from a low to a high value for

a particular value of incubation time. However, magnetization increases gradually with the incubation time. Their results support the phase separation scenario, i.e., coexistence of ferromagnetic metallic and charge-ordered insulating phases. The abrupt increase of the resistivity for a particular value of time was understood in terms of the rapid growth and percolation of the charge-ordered insulating phase (5). Babushkina *et al.* (6) also observed a slow relaxation of the resistivity from a high to a low value with incubation time in the phase-separated $(\text{La}_{0.5}\text{Nd}_{0.5})_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ compound. It is not clear whether such a time-dependent resistivity change is the generic behavior of the phase-separated systems. Recently the Cr-substituted $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ system received attention because of the spectacular insulator–metal transition found under $H = 0\text{ T}$ in these compounds (7), whereas a magnetic field more than 27 T is necessary to induce insulator–metal transition in the undoped phase (8). With this background, the $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ system was further investigated, showing phase separation into ferromagnetic metallic and charge-ordered insulating regions (9–11). Our attention in the present letter is focused on the lightly doped oxide $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.99}\text{Cr}_{0.01}\text{O}_3$, which surprisingly showed a larger magnetoresistance when the sample is field cooled than when zero field cooled (12). In this Rapid Communication, we report a rather unusual phenomenon for this compound: starting from the insulating behavior of this oxide in absence of a magnetic field, the resistivity is lowered in a magnetic field in the first step as shown perviously (12) but the resistivity is unstable and increased by several orders of magnitude upon thermal cycling in presence of a magnetic field.

The polycrystalline $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.99}\text{Cr}_{0.01}\text{O}_3$ was synthesized by mixing the oxides Pr_6O_{11} , CaO , MnO_2 , and Cr_2O_3 in stoichiometric proportions. The powder, first heated at 1000°C with intermediate grindings, was pressed into the form of bars with dimensions $4 \times 4 \times 10\text{ mm}^3$. The

sample was then sintered in air at 1500°C for 12 h, slowly cooled down to 800°C, and finally quenched to room temperature.

Four-probe resistivity on a bar of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.99}\text{Cr}_{0.01}\text{O}_3$ under $H = 4\text{ T}$ was measured using the Quantum Design Physical Properties Measuring System. Magnetization under $H = 4\text{ T}$ on another piece of the same compound was measured using the Quantum Design Superconducting Quantum Interference Device. The rate of cooling and warming was kept at 3 K/min for both measurements.

The top panel of Fig. 1 shows the resistivity of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.99}\text{Cr}_{0.01}\text{O}_3$ under $H = 4\text{ T}$. The curve marked 1 was obtained by cooling the sample from 300 to 5 K in presence of $H = 4\text{ T}$ (field-cooled) and warming back to 300 K. The resistivity exhibits a clear hysteresis behavior in the temperature range $\approx 90\text{--}250\text{ K}$, having lower values while cooling and higher values while warming. This hysteresis behavior in the resistivity is the consequence of the incommensurate–commensurate nature of charge-orbital wave vector (q) (12). After the first cycle, the temperature was reduced to 250 K and the sample was subjected four times to thermal cycling between 250 and 10 K. The number of cycles are denoted in the plot. Surprisingly, the resistivity below 170 K increases each time upon thermal cycling and becomes weakly temperature dependent below 30 K. The resistivity at 10 K increases by more than three orders of magnitude between the first and fourth cycles and ρ below 60 K increases beyond our experimental limit in the fifth cycle. It is also interesting to note that above 170 K all the curves overlap each other except the cooling branch of the first curve. We also investigated the effect of thermal cycling on the parent compound $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ under $H = 4$ and 7 T. However, we could not observe any change in the resistivity because the insulating state of this compound is stable under these field values and the resistivity below 100 K exceeds more than $10^6\ \Omega\text{ cm}$, which is beyond our measurements limit. This difference is mainly explained by the fact that the undoped phase is perfectly charge ordered, whereas Cr doping partially destroys charge ordering and induces phase separation as previously shown (9–12). As a consequence ferromagnetic clusters are formed in the charge-ordered antiferromagnetic matrix of the Cr-doped phase, and this phase separation will play an important role in the thermal cycling phenomena.

Because of the large variation in the resistivity upon thermal cycling found above in the Cr-substituted compound, we could anticipate a large change in magnetization. The bottom panel of Fig. 1 shows $M(T)$ measured under five cycles and the inset shows the low-temperature part of $M(T)$ in an expanded scale. The inset clearly shows that the magnetization decreases upon thermal cycling. Earlier work (12) established that isolated ferromagnetic clusters of few tens of nanometers size develop in the charge-ordered

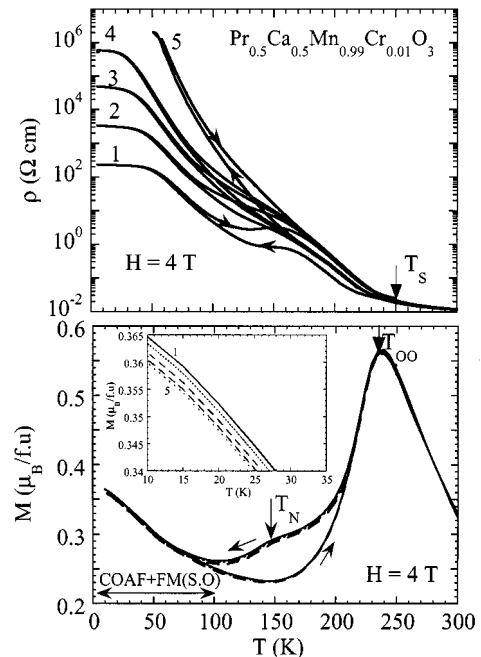


FIG. 1. (Top) Resistivity of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.99}\text{Cr}_{0.01}\text{O}_3$ under $H = 4\text{ T}$ for five thermal cycles. T_S , starting temperature for thermal cycling. Arrows indicate the direction of temperature sweep. (Bottom) Magnetization under $H = 4\text{ T}$ in five thermal cycles. T_{00} , Structural transition due to charge-orbital ordering; T_N , Antiferromagnetic ordering temperature; CO, charge ordering; FM(S,O), short-range ferromagnetic ordering. (Inset) Low-temperature magnetization in an expanded scale.

matrix at low fields ($H < 0.1\text{ T}$) below 30 K. At higher magnetic fields such as $H = 4\text{ T}$, these clusters are partially aligned and ferromagnetic correlations among them extend up to 100 K, leading to increases of M below 100 K. In addition, spin canting in the charge-ordered matrix can also contribute to the rise of M below 100 K.

In Fig. 2 we plot the resistivity at 10 K ($\rho_{10\text{ K}}$) vs. the magnetization at the same temperature ($M_{10\text{ K}}$) for each cycle. The resistivity at 10 K in the fifth cycle, which is beyond our experimental limit, is arbitrarily assigned a value of $10^7\ \Omega\text{ cm}$. While the resistivity increases by five orders of magnitude between the first and fifth cycles, the magnetization decreases only by 1.2%.

In order to eliminate the possibility that the observed increase of the resistivity is not due to the elapse of time during measurement, we carried out the time dependence of the resistivity on a piece of sample that had not undergone thermal cycling earlier. The sample was cooled from 300 to 5 K under $H = 4\text{ T}$ and the resistivity at 5 K was measured as a function of time over 2 h. Figure 3 shows the result. We find that the isothermal resistivity initially decreases rapidly and then slowly as a function of time, which is in contrast to the thermal-cycling-induced effect. This isothermal effect is due to the slow growth of ferromagnetic clusters

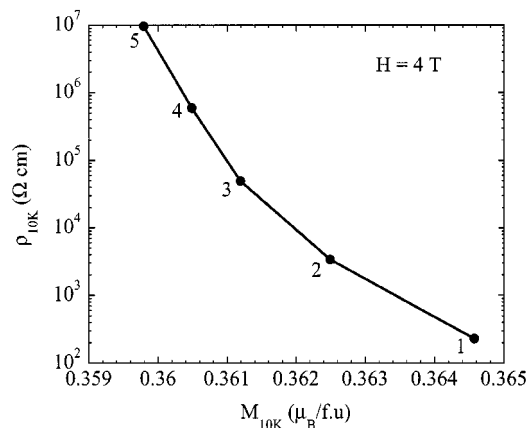


FIG. 2. Dependence of resistivity at 10 K (ρ_{10K}) on magnetization at 10 K (M_{10K}) under five thermal cycles.

at a constant temperature and was also observed in $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.98}\text{Cr}_{0.02}\text{O}_3$ by Kimura *et al.* (10). However, the growth of ferromagnetic clusters does not explain the origin of the thermal-cycling-induced effect. Then, what could be the origin of the observed effect?

It has been indeed shown earlier (12) that field cooling is more effective in lowering resistivity than zero field cooling. Field cooling, apart from aligning ferromagnetic clusters, also breaks the charge-ordered antiferromagnetic matrix into domains due to random field effects (10,12). Under $H = 4$ T, antiferromagnetic domains acquire a finite magnetic moment along the field direction due to spin canting. Electrical conduction in this compound is due to hopping or tunneling of charge carriers between antiferromagnetic domains with a net magnetization and between ferromagnetic clusters. The antiferromagnetic domains are also more strained than ferromagnetic clusters because of the Jahn–Teller distortion of Mn^{3+}O_6 octahedra. Changes in intra(antiferromagnetic)domain or interdomain strains could affect the magnetic structure and resistivity through spin-charge–lattice coupling (2). The higher the strain, the

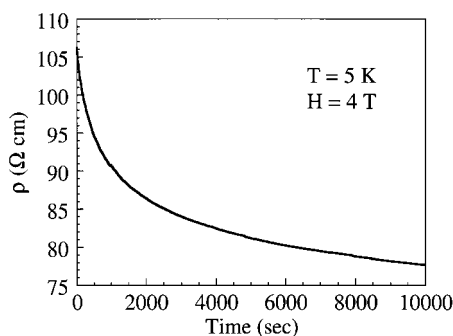


FIG. 3. Relaxation of the isothermal resistivity of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.99}\text{Cr}_{0.01}\text{O}_3$ under $H = 4$ T after cooling from 300 to 5 K.

higher the resistivity. Millis *et al.* (13) showed that biaxial compressive strain to Jahn–Teller distortion of Mn^{3+}O_6 octahedra leads to strong electron–phonon coupling and localization of charges. It is likely that the Jahn–Teller distortion in intradomain and/or interdomain regions increases with thermal cycling, leading to localization of charges, the slowing down of the tunneling/hopping rate, and hence an increase in resistivity. This strain-induced charge localization could possibly explain why the resistivity changes by more than five orders of magnitude, whereas the magnetization decreases by only 1.2%.

In conclusion, we report for the first time that the resistivity of the phase-separated manganite $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.99}\text{Cr}_{0.01}\text{O}_3$ under a magnetic field is unstable and increases by several orders of magnitude with thermal cycling. However, the magnetization decreases only by 1.2%. We suggest that the increase of strain due to the Jahn–Teller distortion is most likely at the origin of the observed effect. Our preliminary investigations on other manganites, for instance, doped with Co and Ni instead of Cr, suggest that similar phenomena could also be observed in other phase-separated manganites. Further studies are in progress to understand these phenomena.

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