

Magnetization steps in the phase-separated Cr-doped $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ compounds

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The manganite $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ has a CE-type antiferromagnetic-insulating (AFI) ground state at low temperatures. This compound undergoes a charge-ordering (CO) transition at $T_{\text{CO}} \sim 250$ K followed by a paramagnetic to AFI (orbital-ordered) OO phase transition at $T_N \sim 170$ K. The ferromagnetic (FM) double-exchange interaction between Mn ions is quenched by such a CO effect. Upon Cr doping, as in single crystals of $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.96}\text{Cr}_{0.04}\text{O}_3$, suppression of the quenched CO-OO state occurs at $T_C \sim 140$ K and is accompanied by a FM-metal-insulator transition. These Cr-doped materials have a low temperature ground state comprised of a mixture of 20–30 nm domains of the FM phase embedded in the CO-OO matrix, as inferred from Lorentz microscopy. Our results show that these Cr-doped materials undergo a field-dependent magnetic transition in a large range of temperature $T < 50$ K, signed by a pronounced magnetization step in $M(H)$ virgin curves. Moreover, from several isothermal hysteresis $M(H)$ curves, we have observed that the FM state remains at $H \rightarrow 0$ and does not collapse back to the AFI state in $M(H)$ cycles performed up to 18 T and $T < 50$ K. These results are different from those found in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ compounds, where the induced FM state by H collapses back to AFI at low H . At 1.4 K, the $M(H)$ virgin curves exhibit a sharp $\Delta H \sim 0.1$ T magnetization step at $H_j \sim 4.3$ T, which is followed by saturation of $M(H) \sim 110$ emu/g in magnetic fields up to $H = 18$ T. The temperature dependence of H_j was found to obey an exponential decay up to $T \sim 50$ K. Such a temperature dependence of H_j indicates that the magnetization steps may not be related to a classical metamagnetic transition, as has been proposed for these manganite compounds. © 2004 American Institute of Physics. [DOI: 10.1063/1.1687226]

The charge-ordered state in manganites with the perovskite structure and the half-doped general formula $\text{Ln}_{0.5}\text{A}_{0.5}\text{MnO}_3$ (Ln=La, Pr, Sm, and Nd; A=Sr and Ca) exhibit a rich variety of intriguing physical phenomena such as charge, orbital, and spin orderings, and magnetic field and current driven transitions.^{1–4} Moreover, substitutions on the Mn site are found to be an effective way to gradually modify the charge-orbital-ordered (CO/OO) insulating antiferromagnetic (AFI) state, along with changes in both temperature (T) and magnetic field (H).^{5,6} It has been reported that a small amount ≤ 0.07 of Cr substituted on Mn sites of the CO/OO $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ manganites has a major influence on both magnetic and transport properties.^{5,6} The compound $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ has a CO/OO ground state with $T_{\text{CO}} \sim 250$ K followed by an AFI phase below $T_N \sim 170$ K. A few percent of Cr substitution induces a ferromagnetic-metallic (FMM) phase at lower temperatures $T_{\text{M}} < 140$ K and suppresses the CO/OO state.^{5,6} Lately, it has been proposed that upon cooling the impurity-doped manganites exhibit a struc-

tural phase separation induced by disorder, with the coexistence of several short-range OO/CO AFI phases and small FMM regions with slightly different crystallographic structures.^{6,7} In fact, transmission electron and Lorentz microscopy studies revealed that 20–30 nm nanodomains of the FMM phase exist embedded in the CO/OO matrix even at $T = 20$ K in Cr-doped $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ compounds, in complete agreement with the coexistence of AFI and FMM inferred by means of transport and magnetic properties.³

The understanding of the reported physical properties has been associated with the idea of the competition of different structural, electronic, and magnetic phases; the so-called phase separation (PS) scenario. Within this context, theoretical and experimental works on manganites revealed an electronic PS between clusters of FMM and CO/OO AFI phases.^{8,9} The PS scenario has been also invoked in order to explain the abrupt magnetization steps (MS) observed in manganites.^{4,10} Particularly in Mn substituted manganites, such a magnetic field induced first-order transition suggests

that the two phases coexist at both low T and H . It has been raised that the observed MS in these manganites are associated with a metamagnetic transition.^{4,10} In these disordered manganites the slightly different unit cells of the FMM and CO/OO AFI phase generate strains at the interface regions, similarly to the strain accommodation observed in martensitic phase transitions.^{4,11} Moreover, it has been observed that such MS exhibit features of a martensitic phase transition as the important cycling effects.^{4,12} Temperature cycles also reveal that the magnetic field at the step field (H_j) increases appreciably and that the saturation moment decreases with increasing thermal cycles, suggesting that a training effect stabilizes the CO/OO AFI phase in detriment of the FMM phase.^{4,12} This observation allowed for a consistent association with the cycling effects observed in martensitic transitions, where thermal cycling across the transition is known to inhibit the transformation.^{4,12}

In the present work we have investigated the magnetic and transport properties of single crystals of $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($0.00 \leq x \leq 0.07$). A single field-dependent magnetization step at H_j has been observed only for single crystals with Cr concentration $x=0.04$ and for $T < 50$ K. In addition, the steps were found to have their counterpart in transport measurements where an appreciable decrease of the electrical resistance occurs at $H \sim H_j$. By computing the values of $H_j(T)$ at different temperatures, we were able to build a $H_j(T)$ phase diagram. The experimental data support the existence of an inhomogeneous ground state comprised of at least two different phases (FMM and CO) in which a martensitelike phase transition of the CO phase at low temperatures is more likely to occur than a classical metamagnetic transition.

The single crystals studied in this work were grown by the floating zone method.⁶ Magnetization $M(T, H)$ measurements were performed using a superconducting quantum interference device (SQUID) magnetometer from quantum design in applied fields $-7 \leq H \leq 7$ T and a homemade force magnetometer ($-18 \leq H \leq 18$ T). The magnetic field has been applied parallel to the ab plane of the single crystals. The $M(H)$ curves were measured following the sequence: (1) the samples were first zero-field cooled from the room temperature down to the desired T ; (2) the H sweep was performed. This procedure was repeated for several T between 100 and 1.4 K. The temperature dependence of $M(T, H)$ was inferred by zero-field-cooled (ZFC) and field-cooled (FC) curves obtained from 5 to 300 K in applied magnetic fields to 1 kOe. Four-wire dc electrical resistivity $\rho(T, H)$ measurements were performed in the temperature range $5 \leq T \leq 300$ K and $0 \leq H \leq 7$ T using the SQUID magnetometer and Keithley current source and voltmeter. The $\rho(H)$ curves were obtained following the same procedure described above for $M(H)$ measurements.

The $\rho(H)$ and $M(H)$ data for the single crystal with $x=0.04$ at $T=7.5$ K are shown in Fig. 1. The features of the $\rho(T, H)$ curves have their counterpart in the $M(H, T)$ data. At low H , the $\rho(T)$ data show a smooth decrease of the electrical resistivity up to $H_j \sim 2.5$ T, where a colossal negative magnetoresistance effect ($\sim 90\%$) develops abruptly, in close resemblance with the step observed in the $M(H)$ data.

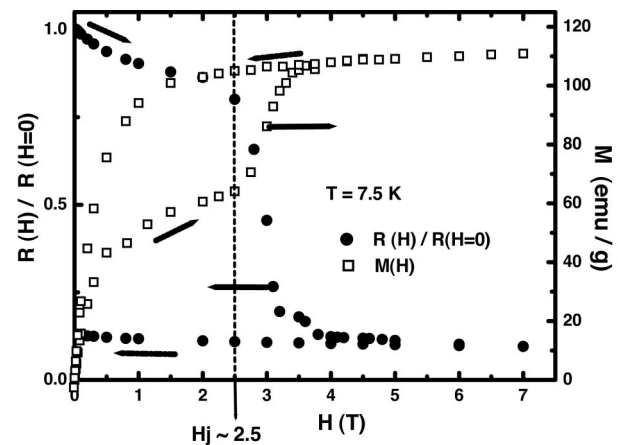


FIG. 1. Magnetic field dependence of the normalized electrical resistivity ρ (left, full circles) and magnetization (right, open squares) at $T=7.5$ K, measured in ZFC mode with increasing (\bullet) and decreasing magnetic field (dashed arrows), for a $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x=0.04$) single crystal.

This low resistivity state was found to be nearly field independent for $H > H_j$ and is preserved in the decreasing branch of the curves. Similar results were obtained in $\rho(T, H)$ curves taken in temperatures up to ~ 25 K and indicate, due to the occurrence of an appreciable magnetic hysteresis, a coexistence of different phases in this compound.

The field dependence of the magnetization $M(H)$ at various measuring T for three single crystals with $x=0.02$, 0.04 , and 0.07 is displayed in Fig. 2. A pronounced single step of the magnetization is observed at a well defined magnetic field $H_j(T)$ for the sample with $x=0.04$. This field-dependent transition was found to occur in a wide range of temperature $1.4 \leq T \leq 50$ K. The magnetic moment exhibits nearly a twofold increase at H_j , jumping from $M \sim 60$ emu/g ($H_j \sim 4.36$ T) to ~ 110 emu/g ($H \sim 4.46$ T) at $T=1.4$ K, a magnitude practically preserved for temperature as high as $T=50$ K. Moreover, the transition width ΔH , defined as the magnetic field interval in which the magnetiza-

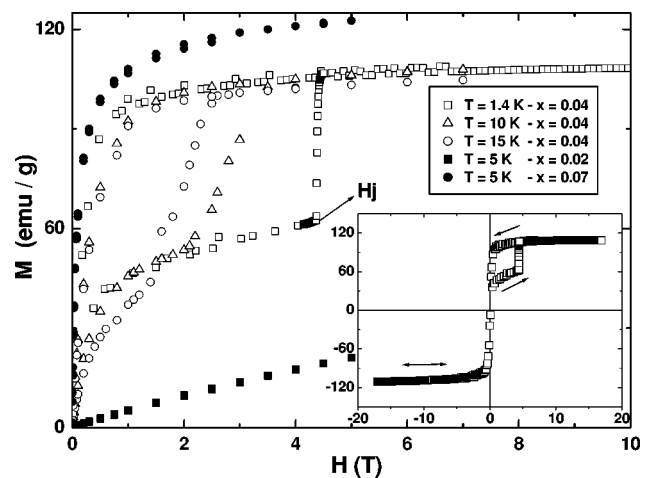


FIG. 2. Field dependence of the magnetization for $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($0.00 \leq x \leq 0.07$) single-crystal samples measured at $T=1.4$, 10 , and 15 K for $x=0.04$ (open symbols) and $T=5$ K for both $x=0.02$ and 0.07 samples (full symbols). The inset shows the $M(H)$ data taken at $T=1.4$ K and for $-18 \leq H \leq 18$ T.

tion step occurs, was found to increase with increasing temperature: it is considerably sharp ($\Delta H \sim 0.1$ T) at $T = 1.4$ K, where $H_j \sim 4.4$ T, and assumes values as high as $\Delta H \sim 1.4$ T at 10 K with $H_j \sim 2.1$ T. Further increasing in H results in saturation of the magnetic moment $M_S \sim 108.5$ emu/g, a value preserved for H to 18 T, as observed in the virgin curve measured at 1.4 K (see the inset of Fig. 1). In fact, all $M(H, T < 50$ K) exhibit similar values of the saturation magnetization. For decreasing magnetic fields, the $M(H)$ curves do not collapse back to the increasing ones (AFI state) even for $H \rightarrow 0$. In the negative H branch of the $M(H)$ curves no magnetization steps are observed in the whole T range investigated (H down to -18 T), as shown in the inset of Fig. 1. We have also investigated the cycling effects on $M(H)$ measurements. The data collected at 10 K (not shown) indicate that cycling effects are pronounced for the two initial cycles and that further cycling (up to 4) results in no appreciable changes. The experimental data revealed that the main effect of increasing the number of cycles is a progressive decrease of the magnetization $M(H_j)$ while both M_S and H_j were found to be cycling independent.

The occurrence of such MS requires information about the effect of Cr doping upon the $M(T)$ data. Within this context, it has been reported that the partial Cr substitution for Mn in $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ induces a FMM state below $T \sim 140$ K in samples with $x > 0.02$. In addition, it has been found that the volume fraction of the FMM phase increases appreciably with increasing Cr content up to $x \sim 0.07$.^{7,13} In the present study, the $M(H)$ measurements performed in both samples with $x = 0.02$ and 0.07 revealed that the MS are absent, at least for applied magnetic fields $H \leq \pm 5$ T. This is an indication that the occurrence of the MS depends upon the initial relative volume fraction of the phases and preferably occurs in samples having a Cr content slightly lower than the optimal doping for the maximum FMM phase content.⁷ In fact, for compositions with $x < 0.07$, the PS scenario is more evident in comparison to the $x = 0.07$ ones, where the FMM phase develops fairly fast with decreasing temperature as evidenced by the rapid decrease of the $\rho(T, H)$ data and the lower hysteresis on the $M(T)$ curves.¹³

The step magnetic field H_j for different measuring T , defined as the magnetic field in which a first increase of $M(H)$ is observed, was extracted and pairs (H_j, T) were collected. The (H_j, T) phase diagram is displayed in Fig. 3 and we have found that H_j follows an exponential decay with increasing T . Using different criteria for H_j determination, as, for instance, the H value at the end of the step and the H value at 50% of the step, revealed no significant changes on the exponential behavior. An important point to be considered is that such a behavior is different from the

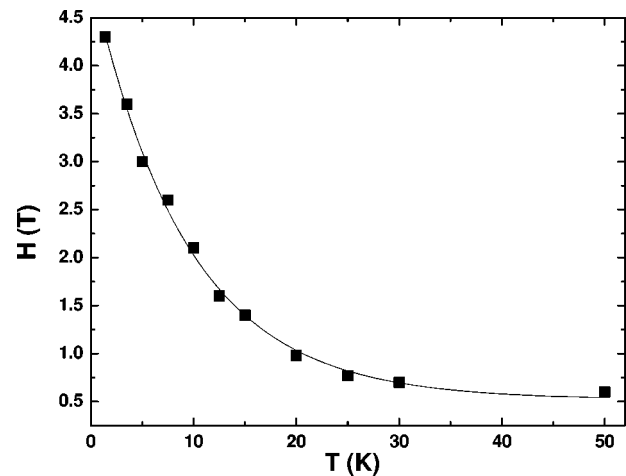


FIG. 3. Temperature dependence of the step magnetic field H_j for the $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.04$) single crystal.

one usually observed in systems which undergo a metamagnetic transition. As in FeCl_2 compounds, for $T < 20$ K (below the critical point) a nearly field-independent behavior is observed.¹⁴ This behavior indicates that the magnetization steps observed in these manganites may not be related to a classical metamagnetic transition.

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