**Multicritical end-point of the first-order ferromagnetic transition in colossal magnetoresistive manganites**

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We have studied the bandwidth–temperature–magnetic field phase diagram of RE0.55Sr0.45MnO3 colossal magnetoresistance manganites with ferromagnetic metallic (FM) ground state. The bandwidth (or equivalently the double exchange interaction) was controlled both via chemical substitution and hydrostatic pressure with a focus on the vicinity of the critical pressure $p^*$ where the character of the zero-field FM transition changes from first to second order. Below $p^*$ the first-order FM transition extends up to a critical magnetic field, $H_c$. It is suppressed by pressure and approaches zero on the larger bandwidth side where the surface of the first-order FM phase boundary is terminated by a multicritical end-point ($p^*=32$ kbar, $T^*=188$ K, $H^*=0$). The change in the character of the transition and the decrease of the CMR effect is attributed to the reduced CO/OO fluctuations.

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Perovskite-type manganites exhibit various fundamental phenomena of current interest including colossal magnetoresistance (CMR), photo- and current-induced insulator to metal transition, first-order ferromagnetic transition and gigantic magneto-electric effect [1]. Most of them are collective effects arising from the strong interplay among the electronic degrees of freedom in the spin, charge and orbital sector which are further coupled to the underlying lattice. One of the most dramatic phase transformations induced by external stimuli is the magnetic field driven paramagnetic insulator (PI) to FM transition. It is observed in a broad range above the Curie temperature and the huge resistivity change associated with the transition is termed as colossal magnetoresistance. In the context of the CMR effect and the orbital order-disorder transition in manganites, the possibility that the first-order nature of phase transitions in three dimensional systems can be preserved in the presence of disorder has recently attracted much interest [2].

Although the detailed mechanism of the CMR effect is still under debate, some of the basic ingredients have already been clarified. Among them the phase competition between the two robust neighboring states, i.e. the charge- and orbital-ordered insulator (CO/OO) and the ferromagnetic metal, is thought to be indispensable [1,3]. In the bandwidth–temperature ($w-T$) phase diagram of CMR manganites with low quenched disorder, these two phases are separated by a first-order phase boundary which can extend to as high temperature as $T \approx 200$ K (see Fig. 1). It is terminated by a bicritical point where the CO/OO and FM transition line ($T_\text{CO}(w)$ and $T_C(w)$, respectively) meet each other. The temperature-induced transition from the high-temperature PI phase to the long-range ordered states on the both sides close to the bicritical point is of first order [4,5,6]. If quenched disorder is introduced to the lattice by alloying rare earth (RE) and alkali earth (AE) atoms on the A-sites with different ionic radius, the phase diagram is strongly modified; the bicritical point is suppressed and a spin-glass state appears between the two ordered phases. On the other hand, $T_{\text{CO}}(w)$ and $T_C(w)$ lines remain of first order for a large variation of the bandwidth [6].

![FIG. 1: (Color online) Bandwidth–temperature phase dia-
gram of RE0.55AE0.45MnO3 manganites near half doping with high level of quenched disorder (reproduced from Tomioka et al. [6]). In contrast to the low-disorder case where $T_{\text{CO}}$ and $T_C$ meet each other and form the so-called bicritical point as represented by dashed lines, the ordered phases are suppressed and an intermediate spin glass phase appears below $T_C$. The phase boundaries corresponding to the high and low-disorder case are shown for the two series, AE=Sr and AE=Ca. In the present study the bandwidth of the FM phase was controlled over the highlighted region by the combination of chemical substitution and hydrostatic pressure.](image)

This situation is shown in Fig. 1 where the typical $w-T$ phase diagram of nearly half doped CMR manganites with large quenched disorder is presented for the
In this study, we aim to map and characterize the $T_C(w)$ phase boundary of $(\text{Sm}_{1-x}\text{Nd}_x)_{0.55}\text{Sr}_{0.45}\text{MnO}_3$ family combining the effect of chemical composition and hydrostatic pressure with a focus on the highlighted region of Fig. 1 where the first-order transition changes to a second-order one. Both methods efficiently vary the effective one-electron bandwidth of these materials as either the increase of the average ionic radius \([6, 10, 11, 12]\) or the application of pressure \([13, 14, 15]\) causes the enhancement of the double exchange interaction responsible for the FM phase. We also investigate the effect of magnetic field on the FM transition and determine the $T_C(H)$ phase boundary at each pressure. All the samples investigated here are single crystals grown by a floating-zone method \([12]\). Resistivity measurements were performed in the standard four-probe configuration and magnetization was detected by using Quantum Design SQUID magnetometer. In both cases the application of hydrostatic pressure was carried out using self-clamping pressure cells with kerosene as pressure-transmitting medium.

The dramatic increase of $T_C$ in presence of magnetic field is characteristic of CMR manganites, especially in the presence of quenched disorder. As shown in Fig. 2(a)-(b), the transition is shifted to higher temperatures at an average rate of $\Delta T_C(H)/\Delta H \approx 0.9\,\text{K/kG} = 9\,\text{K/T}$. Simultaneously, the first-order nature of the transition weakens as clearly reflected by the suppression of the magnetization and resistivity change associated with the transition and also by the reduction of the hysteresis width. For the quantitative analysis we used the latter quantity since it is more reliably obtained from the experimental data. Though no detailed description about the effect of quenched disorder on the thermodynamic and transport properties in the vicinity of a first-order transition is available, we attribute the rounding-off in the resistivity and magnetization curves around $T_C$ to the influence of disorder on the nature of the transition \([16]\). Above a critical magnetic field – $H_{cr} \approx 37.5\,\text{kG}$ in case of $\text{Sm}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$ – the hysteresis completely vanishes and the first-order transition becomes a crossover. (Throughout the paper $T_C$ stands for the zero-field transition temperature, unless field dependence is explicitly indicated.) Similarly, by performing field sweeps at fixed temperatures above $T_C$, the weakening of the first-order character of the field-driven transition is discerned with increasing temperature (see Fig. 2(c)). The hysteresis vanishes above a critical temperature $H_{cr} \approx 165.4\,\text{K}$ for $\text{Sm}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$ at ambient pressure. We call this $(H_{cr}, T_{cr})$ point, the finite-field critical end-point of the first-order FM transition.
The application of pressure increases the magnitude of the double exchange interaction and consequently extends the FM phase to higher temperatures $\Delta T_{C} = \frac{\Delta T_{C}}{p} \approx 2 \text{ K/kbar}$ as discerned in Fig. 2(d) – while the first-order nature of the transition is again reduced. The critical pressure where the zero-field transition becomes of second order is estimated to be $p^{*} \approx 32 \text{kbar}$ for Sm$0.55$Sr$0.45$MnO$_3$. In contrast to $T_{c}\left(p\right)$ which is enhanced by pressure in a parallel manner to $T_{C}\left(p\right)$, the critical magnetic field is suppressed according to $H_{c}\left(p\right) \propto \left(p^{*} - p\right)^{1.05}$ as indicated in Fig. 3. Above the critical pressure $p^{*}$ the finite-field FM transition no longer exists. A systematic series of experiments, similar to those shown in Fig. 2, were used to map the bandwidth–temperature–magnetic field phase diagram for the full range of the compounds.

The evolution of the zero-field $T_{C}$, the hysteresis width representing the first-order character of the transition, and the critical field $H_{c}\left(p\right)$ as a function of pressure are shown in the respective panels of Fig. 3 in the vicinity of the multicritical end-point located at $(p^{*} \approx 32 \text{kbar}, T^{c} \approx 188 \text{K})$. The effect of pressure is nearly identical to that of the chemical substitution as the pressure dependence of the transition temperature for the different compounds fits to the same $T_{C}\left(p\right)$ curve whose tendency is valid for the hysteresis width, as well. We also determined the location of the critical point expressed in terms of the relative composition of Nd and Sm and found $x^{*} \approx 0.33$. The whole pressure–temperature–magnetic field phase diagram is displayed in the upper panel of Fig. 4 while the lower panel shows the hysteresis width over the corresponding area. The surface of the first-order transition is bordered by two lines; the zero-field phase boundary $T_{C}\left(p\right)$ and the finite-field critical endline $(H_{c}\left(p\right), T_{c}\left(p\right))$. With increasing bandwidth the two lines approach each other and the surface is terminated.
by the multicritical end-point. On the larger bandwidth side of the multicritical end-point a second-order FM transition line appears where $T_C(p)$ still monotonically increases with pressure.

The first-order nature of the zero-field FM transition is the strongest for Eu$_{0.55}$Sr$_{0.45}$MnO$_3$ with the lowest transition temperature $T_C \approx 50$K and largest critical field $H_{cr} \approx 74$K. The hysteresis width is $\sim 14.3$K and the resistivity jump across the transition is as large as nine orders of magnitude. This compound is located on the verge of the SG-FM phase boundary and suffers the most from CO/OO fluctuations. Hence, it shows the highest CMR effect among these compounds. The high-temperature state cannot be regarded as a simple paramagnet with disorder in the spin, charge and orbital sector as it is essentially governed by short-range correlations of the CO/OO phase. The finite correlation length of the CO/OO fluctuations (typically a few lattice constant just above $T_C$) can turn the generally continuous PI $\rightarrow$ FM transition to the first-order one.

Recent x-ray diffuse and Raman scattering measurements and optical conductivity experiments have revealed that the CO/OO correlations gradually vanish with increasing temperature. Therefore, towards larger bandwidth, where $T_C$ is remarkably enhanced, the phase fluctuations at the paramagnetic side of the transition become less relevant. The CMR effect is suppressed in accordance with the reduction of the resistivity change upon the transition. Finally, at the multicritical end-point the fluctuation-induced first-order transition is replaced by the usual second-order FM transition. The colossal magnetoresistance does still exist beyond this point but it is less effective due to the rounding-off of the resistivity curves around $T_C$.

In conclusion, by combination of chemical and hydrostatic pressure, we have studied the bandwidth–temperature–magnetic field phase diagram of RE$_{0.55}$Sr$_{0.45}$MnO$_3$ colossal magnetoresistance manganites with large quenched disorder. We have found that the first-order nature of the PI $\rightarrow$ FM transition is robust against the A-site disorder. We have focused on the region where the character of the zero-field FM transition changes from first to second order by variation of the bandwidth. The hydrostatic pressure effectively control the double exchange interaction as the transition is shifted to higher temperatures at a rate of $\Delta T_C(p)/\Delta p \approx 2$K/kbar, while the first-order nature of the transition weakens. Above a critical pressure $p^* \approx 32$kbar the zero-field FM transition becomes continuous. In external magnetic field, the same tendencies are followed except for the nature of the critical end-point. Although the first-order character of the transition is similarly suppressed and eventually vanishes at a critical magnetic field $H_{cr}(p)$, no phase transition exists beyond this point. It becomes a crossover unlike in the zero-field limit controlled by pressure. This finite-field critical end-line approaches the $H=0$ plane according to $H_{cr}(p) \propto (p^* - p)^{\pm 0.05}$. Consequently, the zero-field critical point $(p^*, T^*)$ is a multicritical end-point terminating the surface of the first-order FM phase boundary on the larger bandwidth side. The change in the character of the transition and the weakening of the CMR effect are attributed to the reduced CO/OO fluctuations.

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