Quenched disorder suppression of the first-order magnetic phase transition in manganites

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The role of quenched disorder on the magnetic phase transition of ferromagnetic manganites is investigated through the field and pressure dependence of magnetization around T_C. Our results demonstrate that moderate-small chemical disorder promotes second-order behavior. This can be rationalized on the basis of a simple thermodynamic model in which the magnetic order parameter is coupled to the lattice, this coupling being sensitive to chemical disorder. A plausible microscopic scenario is also discussed.

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INTRODUCTION

A first-order ferromagnetic-to-paramagnetic (FM-PM) phase transition is an atypical phenomenon normally associated with strong coupling among different degrees of freedom. In a ferromagnetic system, coupling between the magnetization M and other order parameters (or between M and some other nonordering variable) can renormalize the Curie temperature T_C and, under certain circumstances, change the order of the magnetic phase transition.[1–4] Interestingly, many of the most exciting electronic and/or magnetic phenomena (large magnetocaloric response in $ErCo_2$,[5] $Mn_{1-x}Fe_xAs$,[6] field-induced structural transitions and magnetoresistance in MnAs,[7] metamagnetism in CoS_2, etc.) appear close to a first-order FM-PM transition.

A paradigmatic example of this behavior is the appearance of colossal magnetoresistance (CMR) around a first-order T_C in manganites, $A_{1-x}A'_xMnO_3$.[8] The flexibility of the perovskite lattice to accommodate different ions at a constant electron doping, provides a rare opportunity to systematically study the problem of a system with a high density of charge carriers with strong coupling to phonons. The intense effort of the last few years showed that CMR is a consequence of the tendency of these systems toward magnetic and/or electric phase separation, due to a strong electron-lattice coupling.[9,10] If large enough, this coupling has been shown to drive the original second-order transition into a first-order one.[11]

On the other hand, together with an average distortion of the lattice, chemical doping at the A site of the perovskite introduces quenched chemical disorder, due to the variance of the ionic radii from site to site.[12] Shortly after the decisive role of electron-phonon coupling for CMR was proposed, Rodriguez-Martinez and Attfield[12] called the attention about the importance of chemical disorder on the physical properties of the system. They proposed the variance of the A-site ionic radii distribution, $\sigma^2=[\langle r_A^2\rangle-\langle r_A\rangle^2]$ as a variable to quantify the disorder inherent to a particular composition. They found that T_C and CMR decrease with σ^2 for small-moderate disorder. The relevance of this effect on the reduction of the critical temperature and CMR itself has been well documented,[13] but studies of the effect over the nature of the magnetic phase transition are scarce. However, these would be important because they could help elucidate the effect of local (rather than average) structural deformations over the global properties of the system. On the other hand, they will provide a test for classical works that treated the effect of *random* quenched impurities on a first-order phase transition.[14,15]

In the first effort of this kind, Burgy *et al.* [16] considered the effect of quenched disorder on the competition between two ordered states. They found that in two dimensions, a small amount of disorder drives the original first-order transition into a second-order one. Later on, they showed that these results can be extended to three dimensions, after recognizing the relevance of cooperative lattice distortions.[17]

Contrary to this result, Kumar and Majumdar[18] solved a disordered double-exchange model for optimally doped ($n\approx 0.3$) manganites and found that chemical disorder promotes first-order phase transitions. Similarly, a combined microscopic calculation and a thermodynamic approach that reproduces chemical disorder on half-doped manganites by Salafranca and Brey[19] concluded that moderate disorder transforms the original second-order transition into a first-order one, with a reduced T_C, in agreement with experimental claims in nearly half-doped $La_{0.54}Ba_{0.46}MnO_3$.[20]

So, there is no consensus at this moment about the role played by quenched chemical disorder on the nature of the magnetic phase transition of manganites.

Here, we present a systematic experimental study aimed to clarify, unambiguously, the role of quenched disorder on the nature of the FM-PM phase transition in ferromagnetic manganites. We will show that disorder suppresses the first-order nature of the transition at the time that reduces the strong susceptibility of T_C to external pressure. A simple thermodynamic model will be presented to account for this behavior. On the other hand, a microscopic interpretation of the experimental results highlights the relevance of cooperation among lattice distortions in the mechanism responsible for two-phase coexistence characteristic of manganites.

EXPERIMENT

In order to investigate the effect of chemical disorder on the nature of the magnetic phase transition, we have synthesized different series of samples of composition $(La_{1-x}Nd_x)_{2/3}(Ca_{1-y}Sr_y)_{1/3}MnO_3$ and $(La_{1-x}Pr_x)_{2/3}(Ca_{1-y}Sr_y)_{1/3}MnO_3$. Different compositions with

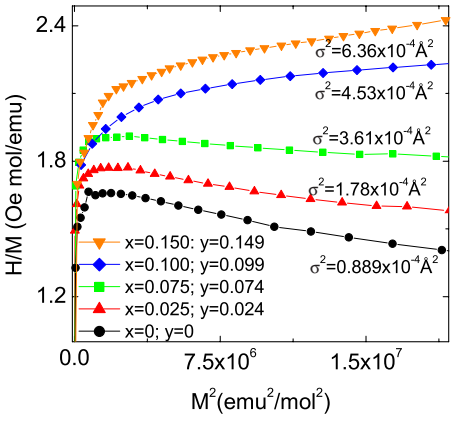

FIG. 1. (Color online) Effect of disorder on the sign of the H/M vs M^2 isotherms at the same equivalent temperature ($=1.02T_C$ for each particular system) for the series $(La_{1-x}Nd_x)_{2/3}(Ca_{1-y}Sr_y)_{1/3}MnO_3$ $\langle r_A\rangle = 1.353$ Å. Only one representative isotherm is presented for each composition for the sake of clarity. The T_C of each sample is, from bottom to top, 264, 261.5, 259, 258.7, and 257 K.

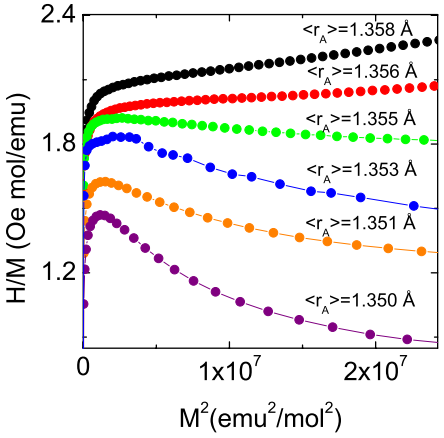

FIG. 2. (Color online) Effect of $\langle r_A\rangle$ in the nature of the magnetic phase transition. Increasing the Pr^{3+}/La^{3+} ratio along the series $(La_{1-x}Pr_x)_{2/3}(Ca_{1-y}Sr_y)_{1/3}MnO_3$, reduces $\langle r_A\rangle$ and drives the original second-order transition into a first-order one. All isotherms correspond to the same equivalent temperature, $1.02T_C$. The absolute value of T_C is, from bottom to top, 241.4, 253.2, 264, 273, 282, and 289 K.

constant $\langle r_A\rangle$ and constant $Mn^{3+}/Mn^{4+}=2$ but different σ^2 were studied. The comparison between Nd^{3+} and Pr^{3+} series allowed us to generalize our results and to rule out any cation-related effect. Single-phase polycrystalline samples were synthesized from high purity precursors by conventional solid-state reactions. High-pressure magnetization was measured in a superconducting quantum interference device magnetometer up to 10 kbar with a Be-Cu cell, using Sn as an internal manometer. T_C for each particular composition was determined from a zero-field cooled (ZFC) magnetization measurement at a magnetic field $H=0.01$ T. Different M vs H isotherms up to 1 T were measured in ZFC conditions around T_C (typically between $0.9T_C<T<1.04T_C$). Following a standard criterion,[21] the order of the transition was determined from the sign of the slope of the H/M vs M^2 isotherms just above T_C. For the sake of clarity, we will only present the results corresponding to $T=1.02T_C$ for each composition.

Ionic radii for oxygen, alkaline earths, and $Mn^{3+/4+}$ ions were taken from Shannon.[22] Values for rare earths are from Jia,[23] all in 12-fold coordination.

RESULTS AND DISCUSSION

One of the key results of this work is presented in Fig. 1. $La_{2/3}Ca_{1/3}MnO_3$ presents a negative slope in the H/M vs M^2 representation, which signals a first-order phase change at T_C, consistent with previous reports.[8,11,24] Increasing σ^2 at a constant $\langle r_A\rangle = 1.353$ Å along the $(La_{1-x}Nd_x)_{2/3}(Ca_{1-y}Sr_y)_{1/3}MnO_3$ series makes the slope of the H/M vs M^2 plot less negative, reaching positive values above a certain value of σ^2. We have observed that the same effect occurs when La^{3+} is replaced by Pr^{3+} instead of Nd^{3+}, and also in $La_{2/3}(Ca_{0.95}Sr_{0.05})_{1/3}MnO_3$, which also undergoes a first-order transition at T_C but with different $\langle r_A\rangle$ ($=1.355$ Å). For compositions with large $\langle r_A\rangle$ and already a second-order phase transition [like, for example, rhombohedral $La_{2/3}(Ca_{0.20}Sr_{0.80})_{1/3}MnO_3$],[11] we have observed that the positive slope of the H/M vs M^2 isotherms becomes even more positive when σ^2 increases.

We have paid special attention to discard any misinterpretation of the data due to a small (undetected) variation of the tolerance factor. First of all, from careful Rietveld analysis of the x-ray powder diffraction, we have verified that the average volume of the samples with constant $\langle r_A\rangle$ and increasing σ^2 remains unchanged for the small-moderate levels of disorder explored in this work. This is clearly against a variation of the average tolerance factor of the system. On the other hand, we have observed that T_C decreases with increasing σ^2, at the time that the transition changes from first to second order. Given that a reduction of the tolerance factor decreases T_C at the time that promotes first-order behavior (see Ref. 11 and Fig. 2 in this work), our results are incompatible with an effect due to a variation of the tolerance factor.

So, our results (Fig. 1) demonstrate, unequivocally, that the first-order FM-PM phase transition in ferromagnetic manganites is progressively suppressed by quenched chemical disorder.

In order to understand this effect, we should first clarify the origin of the first-order phase transition in low $\langle r_A\rangle$ ferromagnetic manganites. The occurrence of a first-order phase transition can be understood using a simple thermodynamic argument, in which the order parameter for the magnetic transition (M) is coupled to the average lattice volume, in a compressible lattice. Close the critical point for the magnetic transition T_C, $M\to 0$, and hence the free energy can be expressed as a power series of M:

$$G = AM^2 + BM^4 + CM^6 + \cdots + K\Delta^2 + \xi M^2\Delta, \qquad (1)$$

where Δ is the average lattice distortion (deviation from the undistorted volume). The fourth and fifth terms of this ex-

pression describe the contribution of the elastic energy and the coupling of the magnetization with the lattice deformation, through ξ, respectively. Taking the volume distortion that minimizes the free energy,

$$\frac{\partial G}{\partial \Delta} = 0 = 2K\Delta + \xi M^2, \tag{2}$$

$$-\xi M^2/2K = \Delta, \tag{3}$$

and inserting this value back in the general equation (1),

$$G = AM^2 + \left(B - \frac{\xi^2}{4K}\right)M^4 + CM^6 + \cdots. \tag{4}$$

If the coupling of the magnetization to the lattice is strong enough ($|\xi|$ large), the term in M^4 of Eq. (4) becomes negative. Given A is not too large and $C>0$, a $4KB<\xi^2$ leads to the appearance of a secondary minimum at $M\neq 0$ above T_C in the evolution of the free energy with the order parameter, i.e., a first-order phase transition at T_C.

It is easy to obtain a more elaborate, formal expression for the free energy within the molecular field approximation,[4] and then to assume a volume dependence of $T_C \propto (1+\xi\Delta)$. This was done in a seminal paper by Bean and Rodbell,[2] but the final expression is completely equivalent to expression (4). For manganites, the lattice distortion Δ is determined by the inverse of the average A-site radius $\langle r_A\rangle^{-1}$ or the mean value of ϕ, being $\langle$Mn-O-Mn$\rangle = 180\text{-}\phi$. In this case, $\xi<0$ and T_C decreases as Δ increases.

Previous results[25] have shown that in $A_{1-x}A'_xMnO_3$, T_C changes more rapidly for highly distorted lattices. Hence, ξ^2 in Eq. (4) must be a decreasing function of $\langle r_A\rangle$. On the other hand, following the results of Fig. 1, ξ^2 is also a decreasing function of σ^2, for a fixed value of $\langle r_A\rangle$. So, following Eq. (4) and these simple relationships, the effect of quenched chemical disorder on the phase transition can be understood as a decoupling between spin and lattice degrees of freedom.

This simple thermodynamic argument demonstrates that although $\langle r_A\rangle^{-1}$ and σ^2 produce a similar decrease of T_C, they actuate through completely different mechanisms, and actually compete with each other. This is an important conclusion that can be derived from this study, but that cannot be anticipated from the reduction of T_C and the metal-insulator transition, T_{MI}, with σ^2. Functional forms of the free energy like Eq. (1), with an order parameter coupled to a nonordering variable or with two coupled order parameters, generate very interesting phase diagrams, with first-order phase transitions and multicritical points, which are relevant to many real systems.[1,19,26]

The next step in our work is to elucidate the microscopic mechanism which couples (decouples) the magnetization and the average (local) lattice distortion to give place to the first (second) order transition at T_C in ferromagnetic manganites.

It is well known that the strong variation of T_C with $\langle r_A\rangle$, or the large isotopic effect[27] in orthorhombic $A_{2/3}A'_{1/3}MnO_3$, cannot be understood on the basis of a pure double-exchange interaction.[28,29] Instead, an inhomogeneous model with coexisting localized (polaronic) and itinerant electrons has been proposed to account for this effect.[11,30] A system which is at

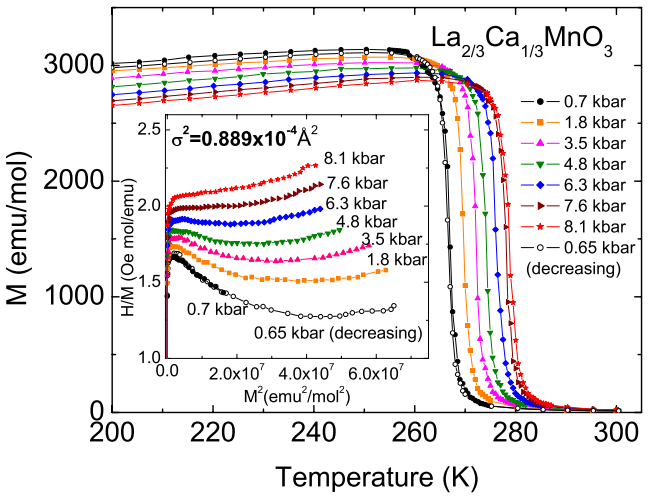

FIG. 3. (Color online) Pressure dependence of the magnetization in $La_{2/3}Ca_{1/3}MnO_3$. T_C (=264 K at $P=0$ kbar) increases with pressure at a rate $\sim$1.4(1) K/kbar. Inset: Pressure dependence of the H/M vs M at $T=1.02T_C$. In this case, first-to-second-order transition occurs at a pressure of $\sim$6.6(2) kbar. Open symbols refer to measurements taken after releasing the pressure (decreasing).

a crossover from polaronic to itinerant electronic behavior is intrinsically unstable relative to segregation into hole-rich, itinerant-electron regions with $\tau_h<\omega_o^{-1}$ and hole-poor polaronic regions with $\tau_h>\omega_o^{-1}$, where τ_h and ω_o^{-1} are the time for an electron to tunnel from a Mn^{3+} to a Mn^{4+} ion and the period of the optical-mode vibration of the MnO_3 array that would localize an electron as a polaron, respectively. Where a $\tau_h \approx \omega_o^{-1}$ is approached, τ_h increases with the depth of the polaronic trap state, and this trap state is deepened by a Jahn-Teller deformation of the site. The orthorhombic crystal symmetry allows a Jahn-Teller deformation, which, if possible, will occur in a cooperative form (neighboring MnO_6 octahedra share a common oxygen) to reduce elastic energy. Reducing $\langle r_A\rangle$ increases the relative volume of the polaronic relative to the itinerant-electron phase, and T_C decreases.[11] In addition, where the change in the number of localized electrons is very abrupt on approaching T_C from below, a first-order magnetic phase transition is predicted at T_C.[11]

Two important consequences can be derived from this model: the polaronic phase increases as $\langle r_A\rangle$ decreases, making the original second-order transition of first-order. This is demonstrated in Fig. 2 (and also in Ref. 11). As $\langle r_A\rangle$ decreases, the slope in the H/M vs M^2 isotherms changes from positive (second order) to negative (first order). This effect has been proven to be general, not related to a particular composition. On the other hand, σ^2 decreases as $\langle r_A\rangle$ decreases in these samples. The decrease of T_C shows then that $\langle r_A\rangle$ is dominant over quenched disorder at moderate-low levels of disorder.

On the other hand, the polaronic phase (larger volume) should be suppressed with pressure, and hence T_C should increase at the time that the first-order transition transforms into a second-order one. To verify this hypothesis, we have measured the H/M vs M^2 isotherms under pressure, slightly above T_C. The results are shown in Fig. 3 for

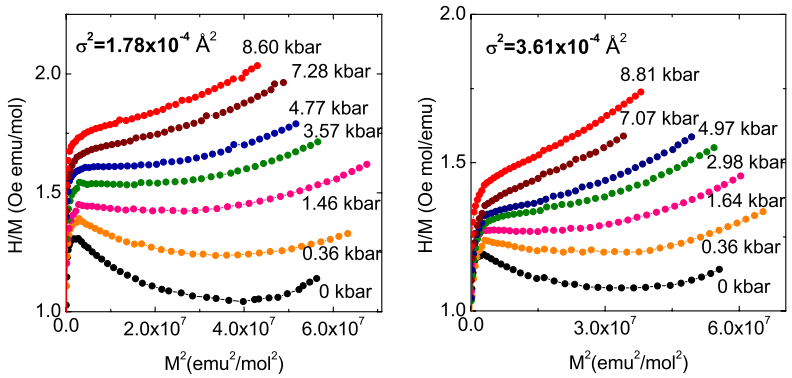

FIG. 4. (Color online) Pressure dependence of the H/M vs M^2 isotherm at $T=1.02T_C$ for two different samples with the same $\langle r_A\rangle=1.353$ Å, increasing disorder. Left: $(La_{0.975}Nd_{0.025})_{2/3}(Ca_{0.976}Sr_{0.024})_{1/3}MnO_3$, $T_C=261.5$ K, $\sigma^2=1.78\times10^{-4}$, $P_C\approx3.7(1)$ kbar. Right: $(La_{0.925}Nd_{0.075})_{2/3}(Ca_{0.926}Sr_{0.074})_{1/3}MnO_3$, $T_C=259$ K, $\sigma^2=3.61\times10^{-4}$, $P_C\approx1.7(1)$ kbar. P_C represents the pressure at which a change from the first- to the second-order transition occurs at T_C.

$La_{2/3}Ca_{1/3}MnO_3$. First-to-second-order transition indeed occurs at a pressure of ~6.6(2) kbar. At this pressure, the first-order transition line at T_C meets the line of second-order transition ($4KB=\xi^2$), defining a tricritical point.[31]

On the other hand, we have determined the effect of pressure in T_C and in the order of the phase transition as σ^2 increases, but keeping constant $\langle r_A\rangle$. The pressure needed to induce a change from the first- to the second-order transition at T_C decreases progressively as σ^2 increases (Fig. 4). That means that the proximity to the tricritical point can be controlled by σ^2 in addition to the external pressure (see the vertical arrows in Fig. 5).

At the same time, the rate of increase of T_C with pressure decreases as σ^2 increases (inset of Fig. 5). Taking into account that the mean value of $\langle r_A\rangle$ is kept constant, these results indicate that the effectiveness of the process responsible for electronic localization (to form polarons) decreases with σ^2.

These experimental results demonstrate that cooperation between the single-site MnO_6 distortions is a key to understand the strong reduction of T_C, and also the existence of a first-order magnetic phase transition in small $\langle r_A\rangle$ ferromagnetic manganites. Strong site-to-site local variations of $\langle r_A\rangle$ will break the cooperativity among the distortions, reducing the extent of the localization, and hence favoring continuous transition at T_C. Consistent with that scenario, the increase in the residual resistivity with σ^2 points to some form of uncorrelated localized (Anderson-like) states. This explains the reduction of CMR and of the absolute magnetization with σ^2 for small-moderate values of disorder.[13,18] Our results are also fully consistent with previous experimental and theoretical works that highlighted the relevance of cooperative lattice distortions.[17,32]

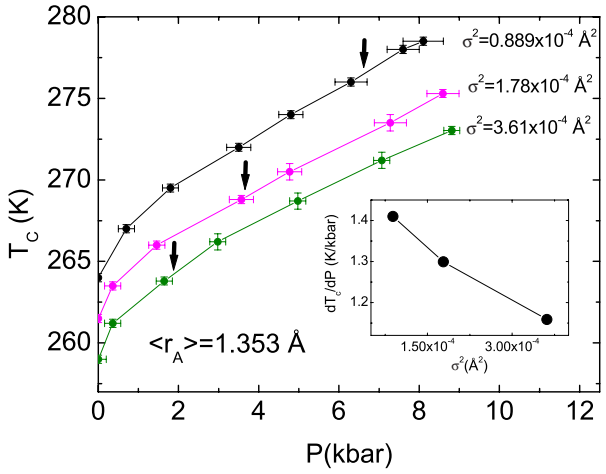

FIG. 5. (Color online) Pressure dependence of T_C for a constant $\langle r_A\rangle$ and different values of σ^2. The arrows mark the crossover from first- to second-order phase transition induced by pressure at each particular composition. Inset: Variation of T_C with P (extracted from the high-pressure linear part) for different σ^2. Note that not only the absolute value of T_C decreases with σ^2 but also its pressure susceptibility.

On the other hand, and given this microscopic scenario, the average lattice distortion Δ of Eq. (1) must be redefined as a cooperative lattice distortion of the MnO_6 octahedra.

Finally, the effect of chemical disorder on the nature of the phase transition of half-doped and nearly half-doped manganites[19,20] could fall in a different category due to the strong orbital ordering presented at these compositions. Disorder will surely produce a collapse of the orbital ordering and could produce first-order transitions, but through a completely different mechanism. This point deserves further investigation.

In summary, we have demonstrated that quenched chemical disorder suppressed first-order magnetic phase transitions in ferromagnetic manganites, which has important consequences on the physical properties of these materials. On the other hand, this study has been proved to be very helpful to elucidate the microscopic role of quenched disorder on decoupling spin and lattice degrees of freedom. We have shown that although the local and average lattice distortions both produce a similar decrease of T_C (both are commonly called "lattice effects"), they are completely different and actually compete with each other.

We also hope that our results will inspire the revision of previously published theoretical works that suggested, contrary to our observation, that chemical disorder could promote first-order behavior in manganites.

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