Abrupt field-induced transition triggered by magnetocaloric effect in phase-separated manganites

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The occurrence at low temperatures of an ultrasharp field-induced transition in phase-separated manganites is analyzed. Experimental results show that magnetization and specific-heat steplike transitions below 5 K are correlated with an abrupt change of the sample temperature, which happens at a certain critical field. This temperature rise, a magnetocaloric effect, is interpreted as produced by the released energy at the transition point and is the key to understand the existence of the abrupt field-induced transition. A qualitative analysis of the results suggests the existence of a critical growing rate of the ferromagnetic phase, beyond which an avalanche effect is triggered.

Mixed valent manganites show a great deal of fascinating properties, arising from the strong interplay between spin, charge, orbital, and lattice degrees of freedom.[1] The most intriguing one is the existence of a phase-separated state, the simultaneous coexistence of submicrometer ferromagnetic (FM) metallic and charge ordered (CO) insulating regions.[2] The phase separation scenario has its origin in the unusual proximity of the free energies of these very distinct FM and CO states, and in the fact that the competition between both phases is resolved in mesoscopic length scales, giving rise to real-space inhomogeneities in the material.

Yet another surprising result more recently found in manganites is the appearance of ultrasharp magnetization steps at low temperatures (below ~ 5 K) in the isothermal magnetization $M(H)$ curves.[3–7] This effect, the field-induced transition of the entire compound from one phase to the other of the coexisting states, is included in the category of metamagnetic transitions.[8] However, unlike the broad continuous transitions expected for inhomogeneous granular systems, in this case it occurs in an extremely narrow window of magnetic fields. These ultrasharp steps were observed in both single crystals and polycrystalline samples, indicating that it is not related to a particular microstructure of the material.

The actual existence of a phase-separated state was recognized as a key parameter for the observation of these magnetization jumps.[7] The effect was first reported in manganites doped at the Mn site, and the disorder in the spin lattice was thought to play a relevant role.[4] However, a similar behavior was also found in $Pr_{0.6}Ca_{0.4}MnO_3$, and the qualitative interpretation of the phenomenon shifted to the martensic character of the phase-separated state.[6] Accommodation strains were shown to be relevant in the stabilization of phase separation,[9,10] but their role in the magnetization steps is not clear, since it is expected that grain boundaries would act as a sort of "firewall" for the movement of the domain walls, stopping the avalanche process. Additionally, despite its in-

trinsic first-order character, the martensitic transformation is spread over a large range of the external parameter driving the transition, the magnetic field in the present case, in strong disagreement with the abrupt character of the transition.

The aim of this investigation is to address a basic question concerning this abrupt field-induced transition: why is this metamagnetic transition so sharp, and what is actually causing it? We report the occurrence of ultrasharp magnetization steps at low temperatures in a prototype phase-separated manganite, which are accompanied by discontinuities in the magnetic-field dependence of the specific heat. Concomitantly with these facts, we found that the field-induced transition is accompanied by a large increase in the temperature of the sample, by dozens of degrees. This feature suggests a mechanism in which the abrupt first-order transition in the whole sample is triggered by the released heat in a microscopic phase transformation. A low-temperature heat controlled magnetization avalanche was previously found in bulk disordered magnets[11] due to the heat released by the FM domain wall motion during the reversal of the remnant magnetization. Also, local heating induced by nonuniform current flow was proposed as the origin of the mesoscopic fluctuations between coexisting phases observed in $La_{0.225}Pr_{0.40}Ca_{0.375}MnO_3$.[12] We propose that in phase-separated manganites the interplay between the growth of the FM phase induced by the magnetic field and the heat generated by this growth is the key to explain the avalanche process leading to an ultrasharp field-induced transition in these inhomogeneous strongly correlated systems.

The particular compound under study is a high quality polycrystalline sample of $La_{0.225}Pr_{0.40}Ca_{0.375}MnO_3$, synthesized by the sol-gel technique. It belongs to the well-known family of compounds $La_{5/8-y}Pr_yCa_{3/8}MnO_3$, whose tendency to form inhomogeneous structures in the range $0.3 \leq y \leq 0.4$ is extensively documented.[13–18] Scanning electron micrographs revealed a homogeneous distribution of grain sizes, of the order of 2 μm. An identification of the magnetic phases
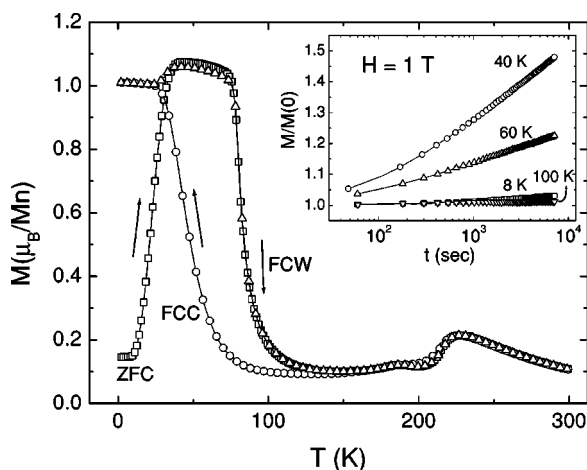
FIG. 1. Temperature dependence of the magnetization, measured with $H=1$ T with zero-field-cooling (ZFC), field-cooled-cooling (FCC), and field-cooled-warming (FCW) procedures. The inset shows the time evolution of the normalized magnetization after ZFC to $T=8$, 40, 60, and 100 K.

of the material can be made through the temperature dependence of the magnetization, $M(T)$. The results were obtained on an extraction magnetometer with a field $H=1$ T, and are shown in Fig. 1. As the temperature is lowered the sample changes from a paramagnetic to a charge-ordered antiferromagnetic state at $T_{CO}=220$ K. Just below, a small kink at 190 K is a signature of the onset of the formation of ferromagnetic clusters.[18] A more robust ferromagnetic phase appears at $T_C=70$ K (90 K on warming), which coexists with the majority CO state in an inhomogeneous phase-separated state.[13] In a temperature window extending from T_C down to a temperature $T_b \simeq 20$ K the magnetization shows considerable relaxation effects, as shown in the inset of Fig. 1, signaling the growth of the FM phase against the CO background. The temperature T_b (which depends on the applied field) can be identified as a blocking temperature; relaxation below T_b is strongly reduced. Additionally, the magnetic state below T_b is highly dependent on the sample magnetic field and cooling history. If the sample is cooled without an applied field [zero-field cooling (ZFC)] the magnetization at 2 K shows a significant low value, which remains unchanged while warming until T_b, above which it shows a continuous increase and merges with the field-cooled-warming curve.

With the application of a large enough magnetic field the low-temperature (below ~ 5 K) zero-field-cooled state is transformed into a FM phase in an abrupt steplike metamagnetic transition. Figure 2(a) shows magnetization measurements as a function of applied field, $M(H)$, measured at $T=2.5$ K. At a certain critical field H_C the entire system changes to a nearly homogenous FM state, which remains stable even after the field is removed. The width of the transition, determined by repeating the measurements with lower field increments, is below 10 Oe. Figure 2(b) shows specific-heat data as a function of applied field $C(H)$ measured by the relaxation method at the same base temperature $T=2.5$ K. As can be readily noticed, a discontinuous transition occurs at approximately the same magnetic field, indicating that a true thermodynamic transition is taking place.
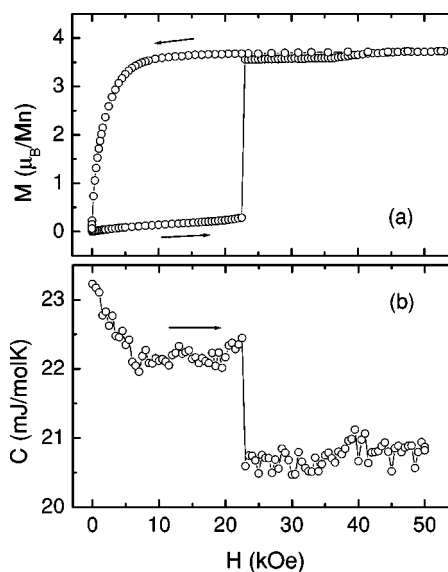

FIG. 2. (a) Field dependence of the magnetization and (b) specific heat, measured at $T=2.5$ K. Both measurements show an abrupt change at the same critical field $H_C \simeq 2.2$ T.

Since the observed transition is first order, it is expected that the latent heat involved should affect the thermodynamic state of the sample, for instance, its temperature. In order to gain some insights on the magnitude of the effect the following experiment was performed: with the sample placed in a vacuum calorimeter with a weak thermal link to the temperature controlled surroundings (kept at 2.5 K), the sample's temperature was measured while the magnetic field was increased, with field increments identical to the data of Fig. 2. The obtained result, plotted in Fig. 3, shows the occurrence of a sudden and huge increase of the sample's temperature, greater than 25 K, at the same critical field of the magnetization jump. Since the relaxation time for temperature stabilization between the sample and the temperature controlled surroundings (of the order of several seconds) is much larger than the internal time constant between the sample and the
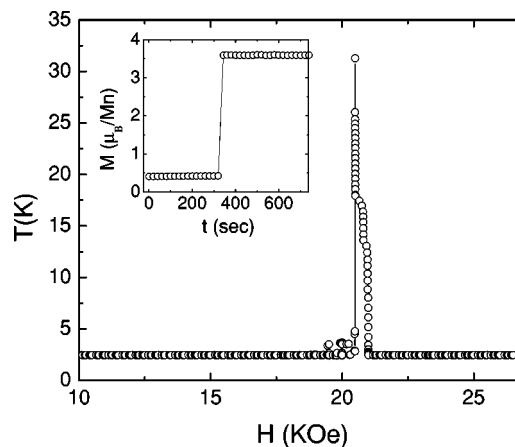

FIG. 3. Field dependence of the sample's temperature showing an abrupt warming from 2.5 to ~ 30 K at $H_C \simeq 2.2$ T. The inset shows a spontaneous magnetization jump, measured with a fixed magnetic field.

sample holder (of the order of milliseconds), the temperature rise measured is intrinsic to the sample. The abrupt increase of the sample's temperature can be then doubtless ascribed to the heat generated when the non-FM fraction of the material is converted to the FM phase. The same experiment was repeated with samples of $La_{5/8-x}Pr_xCa_{3/8}MnO_3$ with different Pr contents, as well as in samples of the series LaNdCaMnO. Whenever a magnetization jump occurs a sizable increase of the sample's temperature was observed. It is also worth mentioning that in the $M(H)$ and $C(H)$ data of Fig. 2 the sample's temperature is in fact not strictly constant; there is also a sudden temperature rise at the field of the step transition, followed by a quick relaxation to the base temperature of the system.

The process which starts with nearly the whole material in the non-FM phase at $T_0 = 2.5$ K and ends with a nearly homogeneous FM state at $T_f \approx 30$ K is conceptually related with the magnetocaloric (MC) effect.[19] The MC effect consists basically in a temperature change ΔT induced by the application of a magnetic field, which, within the approximation of reversible process, is related with the entropy change ΔS generated by ordering the spin lattice. In our case, however, the approximation of reversible adiabatic process is not valid, due to the strong irreversible character of the field-induced transformation. Also, as the phase transition from the CO to the FM phases involves large changes in the magnetic, structural, and electronic properties, which are strongly correlated, the magnetic field affects all the degrees of freedom of the system. This fact makes inapplicable some of the usual basic equations employed in the description of the MC effect. A more realistic approach is to use the conservation of the internal energy during the fast conversion process (hypothesis of adiabaticity). Neglecting small changes of the sample volume, we can make the identity $u_{CO}(T_0) = u_{FM}(T_f, H)$, where u is the internal energy per volume unit. Replacing the whole (irreversible) process by an isothermal plus an isobaric one, we can write

$$u_{CO}(T_0) = u_{FM}(T_0, H) + \int_{T_0}^{T_f} c_p dT, \qquad (1)$$

where c_p is the specific heat of the FM phase at constant pressure. This yields an estimate for the released heat at the field-induced transition given by $\delta q_{rel} = u_{CO}(T_0) - u_{FM}(T_0, H) \simeq \int_{T_0}^{T_f} c_p dT = 48$ J/mol. This estimated value was obtained from specific-heat measurements as a function of temperature performed at zero magnetic field after the sample was transformed to the FM phase by application of a field of 9 T.

The magnetization and specific-heat results, shown in Fig. 2, are macroscopic signatures of a phenomenon which must be understood at a microscopic level. Below the temperature T_b the sample gets into a strongly blocked regime, in which the FM clusters cannot grow against the CO background (see inset of Fig. 1). After zero-field cooling, the sample reaches the blocked state with a small, time-independent, fraction f of FM phase, which can be thought as distributed in isolated regions or clusters surrounded by a CO matrix. The application of an external magnetic field H weakens this frozen-in state, inducing the increase of each cluster of volume v_i in an amount δv_i, which can depend on v_i, T, H, and time. The released heat yielded by this particular process is $\delta Q_{rel} = q_{rel} \delta v_i$. Part of this energy is used to locally increase the temperature of the FM volume v_i, a process that can be considered as instantaneous, taking into account that the thermal conductivity of the FM phase is much greater than that of the CO phase. The remaining energy δQ_{CO} is evacuated through the surrounding CO region. This balance yields

$$q_{rel} \delta v_i = c_p v_i \delta T + \delta Q_{CO}. \qquad (2)$$

Once a process involving a change of the local FM fraction happens, the further evolution of the system is determined by the interplay between the rates at which the system is generating heat and the rate at which the CO phase is releasing it. When the former is greater than the latter, a local temperature rise within the FM region is obtained. If this temperature reaches values beyond the blocking temperature corresponding to the applied field H the system becomes critical, in the sense that the adjacent CO regions, which in turn will increase their local temperature too, become highly unstable. These unstable CO regions are now easily transformed to the FM state, releasing heat, and so on, inducing an avalanchelike chain reaction. At the end, all regions which have ferromagnetism as its equilibrium state at $T = T_f$ and field H had been converted from CO to FM. The equilibrium fractions of the coexisting phases at that T and H values then determine the size of the avalanche process.

Following Eq. (2), we can make an estimation of the critical value of the volume change δv_i^{crit} which is needed to turn on the avalanche process. The first condition to be accomplished is that the temperature of the local FM region increases beyond the blocking temperature $T_b(H)$. Assuming that it occurs in a time scale τ and that in this scale the heat transferred to the CO region is negligible, we obtain

$$\delta v_i^{crit}/v_i = \frac{\int_{T_0}^{Tb} c_p dT}{q_{rel}}, \qquad (3)$$

where $T_b(H) \simeq 8$ K at $H_c = 2.2$ T was estimated from ZFC magnetization measurements. This calculation yields $\delta v_i^{crit}/v_i \simeq 0.01$, i.e., almost 1% increase of the local FM volume is needed to initiate the abrupt transition. This condition must be accompanied by another one, related with the time τ in which the volume enlargement occurs. As mentioned above, this time has to be short enough to avoid the heat being released through the surrounding CO region, i.e., the condition $q_{rel} \delta v_i / \tau \gg a_i k \partial T / \partial z$ must hold, where a_i is the area of the cluster surface, k is the thermal conductivity of the CO phase, and z is a local spatial coordinate. A crude estimation of τ can be done assuming that, within the adjacent CO region, the temperature decays from $T_b(H)$ to T_0 in a length $\delta v_i^{1/3}$ and taking into account that typical low-temperature values for k could range between 0.1 and 1 W/(mK). These assumptions give, for instance, τ
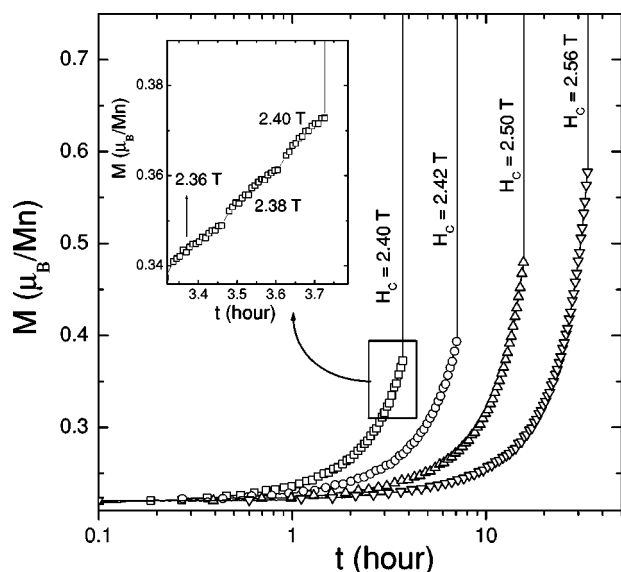
FIG. 4. Time dependence of the magnetization during a magnetic field sweep, for different waiting times between consecutive field increments: t_w=7.5 (squares), 15 (circles), 30 (up triangles), and 60 min (down triangles), at T=2.5 K. The inset shows an enlarged portion of the region just before the magnetization jump.

$\ll 10^{-11}$–10^{-12} s for clusters of volume $v_i=(50 \text{ nm})^3$, and predict a critical rate $\delta v_i^{crit}/\tau \propto v_i^{1/3}$. Therefore, we estimate that thermal processes that happen within a narrow time window, involving a 1% increase of the local FM regions, are needed to initiate the abrupt field-induced transition, the critical rate scaling as the linear size of the FM cluster.

The occurrence of the step transition is then governed by the probability of such an event, once the magnetic field has yielded the crossover between the free energies of the coexisting phases. One way to modify the avalanche probability is allowing the system to relax before reaching the critical state. Allowing relaxation an increase of the FM fraction as a function of the elapsed time occurs, and consequently the value of the δv_i^{crit} needed to turn on the process should also increase. This would be reflected on the dependence with the elapsed time of the critical field H_C at which the jump occurs. To verify this hypothesis we have measured the time dependence of the magnetization during a field sweep, $M(H,t)$ at 2.5 K, starting with H=1.9 T and a waiting time t_w at fixed H before changing to the next field value. In Fig. 4 we show the M vs t curves obtained for different values of t_w, confirming the above presumption: for larger t_w the magnetization jump occurs at higher critical fields. As a remarkable result, we observed that in most cases the step transition occurs spontaneously within the time interval where the field was unchanged. This fact suggests unambiguously that the width of the step transition, beyond any experimental resolution, is strictly zero. The inset of Fig. 3 shows a spontaneous (as opposed to field-induced) magnetization jump, which happens at a fixed field and temperature values. The occurrence of spontaneous magnetization jumps in phase-separated manganites was also reported by another group.[20]

The fact that the step transition can be reached spontaneously while the external parameters (H and T) are kept constant indicates that the abrupt transition is truly connected with the probability of occurrence of certain microscopic process, which within the above described scenario is a particular enlargement of the FM phase. However, this process will initiate the avalanche only when the local increment of the FM phase is large and fast enough to yield the appropriate increase of the local temperature through a magnetocaloric effect. Figure 4 and its inset clearly show that not any enlargement process is able to trigger the step transition. The relaxation effects displayed by the system before the occurrence of the magnetization jump indicate that the system can in fact increase its FM phase fraction without initiating the avalanche, i.e., there are FM regions that start to become unblocked for field values just below the critical field, increasing their local volume by overcoming energy barriers. For instance, the curve for t_w=60 min (with H_C=2.56 T) shows a sizable increase of the FM fraction before the occurrence of the magnetization jump. From inspection of Fig. 4, it is likely that for larger values of t_w larger values of the FM fraction before the jump would be obtained. The waiting time t_w is a key parameter to determine the energy barrier values for which the system is blocked. Eventually, for an extremely large value of t_w the whole system would behave as unblocked and the $M(H)$ curve obtained in this hypothetical situation would display a continuous metamagnetic transition behavior, without jumps. Therefore, once the value of the minimal H_C corresponding to the fastest experiment is established, the limit temperature above which the step transition no longer occurs is determined by the blocking temperature corresponding to this field, $T_b(H_C)$. This suggests why the magnetization jump occurs only below a very specific temperature,[5] above which the system overcomes the energy barriers without turning on the avalanche process.

In conclusion, we have presented evidence that the low-temperature abrupt field-induced transition occurring in phase-separated manganites is intimately related with the sudden increase of the sample temperature at the first-order transition point, a feature that is crucial for the understanding of the phenomenon. We proposed a simple model in which the close interplay between the local increase of the FM phase and the heat released in this microscopic transformation can turn on the avalanche leading to the observed step-like transition. Within this framework, the entity which is propagated is heat, not magnetic domain walls, so the roles of grain boundaries in ceramic samples or strains which exist between the coexisting phases are less relevant. The observation of spontaneous transitions gives additional support to that view, demonstrating that the step transition is not only the result of a crossover between macroscopic free energies induced by the magnetic field, but must be triggered by a microscopic mechanism that initiates the avalanche process. Additionally, we have established that a critical relative increment of a FM region or cluster is needed for the system to reach the "chain reaction" state, i.e., larger initial FM fractions require larger critical fields to *turn on* the process, a feature previously observed.[5] Finally, it must be emphasized that the basic condition for the occurrence of the abrupt transition is that the system must reach the low-temperature

regime in a strongly blocked state. At temperatures just a few degrees higher the abrupt steplike transition no longer occurs, and it is replaced by a standard continuous metamagnetic transition.[5] In summary, we propose that some microscopic mechanisms promote locally a FM volume increase, which yield a local temperature rise, and trigger the observed avalanche process.

[1] M. B. Salamon and M. Jaime, Rev. Mod. Phys. **73**, 583 (2001).

[2] E. Dagotto, T. Hotta, and A. Moreo, Phys. Rep. **344**, 1 (2001).

[3] S. Hébert, V. Hardy, A. Maignan, R. Mahendiran, M. Hervieu, C. Martin, and B. Raveau, J. Solid State Chem. **165**, 6 (2002).

[4] S. Hébert, A. Maignan, V. Hardy, C. Martin, M. Hervieu, and B. Raveau, Solid State Commun. **122**, 335 (2002).

[5] R. Mahendiran, A. Maignan, S. Hebert, C. Martin, M. Hervieu, B. Raveau, J. F. Mitchell, and P. Schiffer, Phys. Rev. Lett. **89**, 286602 (2002).

[6] V. Hardy, S. Hebert, A. Maignan, C. Martin, M. Hervieu, and B. Raveau, J. Magn. Magn. Mater. **264**, 183 (2003).

[7] S. Hébert, A. Maignan, V. Hardy, C. Martin, M. Hervieu, B. Raveau, R. Mahendiran, and P. Schiffer, Eur. Phys. J. B **29**, 419 (2002).

[8] E. Stryjewski and N. Giordano, Adv. Phys. **26**, 487 (1977).

[9] V. Podzorov, B. G. Kim, V. Kiryukhin, M. E. Gershenson, and S-W. Cheong, Phys. Rev. B **64**, 140406 (2001).

[10] N. D. Mathur and P. B. Littlewood, Solid State Commun. **119**, 271 (2001).

[11] M. Uehara, B. Barbara, B. Dieny, and P. C. E. Stamp, Phys. Lett. **114A**, 23 (1986).

[12] V. Podzorov, C. H. Chen, M. E. Gershenson, and S-W. Cheong, Europhys. Lett. **55**, 411 (2001).

[13] M. Uehara, S. Mori, C. H. Chen, and S-W. Cheong, Nature (London) **399**, 560 (1999).

[14] M. Uehara and S-W. Cheong, Europhys. Lett. **52**, 674 (2000).

[15] K. H. Kim, M. Uehara, C. Hess, P. A. Sharma, and S-W. Cheong, Phys. Rev. Lett. **84**, 2961 (2000).

[16] A. M. Balagurov, V. Y. Pomjakushin, D. V. Sheptyakov, V. L. Aksenov, N. A. Babushkina, L. M. Belova, O. Y. Gorbenko, and A. R. Kaul, Eur. Phys. J. B **19**, 215 (2001).

[17] V. Kiryukhin, B. G. Kim, V. Podzorov, S-W. Cheong, T. Y. Koo, J. P. Hill, I. Moon, and Y. H. Jeong, Phys. Rev. B **63**, 024420 (2001).

[18] P. Levy, F. Parisi, M. Quintero, L. Granja, J. Curiale, J. Sacanell, G. Leyva, G. Polla, R. S. Freitas, and L. Ghivelder, Phys. Rev. B **65**, 140401 (2002).

[19] V. K. Pecharsky and K. A. Gschneidner, Jr., J. Appl. Phys. **86**, 565 (1999); J. Magn. Magn. Mater. **200**, 44 (1999).

[20] V. Hardy, A. Maignan, S. Hébert, C. Yaicle, C. Martin, M. Hervieu, M. R. Lees, G. Rowlands, D. M. Paul, and B. Raveau, Phys. Rev. B **68**, 220402 (2003).