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Observation of spontaneous magnetization jumps in manganites

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For certain combinations of temperature and magnetic field, the evolution with time of the magnetization of some phase-separated manganese oxides exhibits a unique steplike feature. This jump in the magnetization is proposed to correspond to a burstlike growth of the ferromagnetic fraction at the expense of the antiferromagnetic component, driven by the evolution of the strains at the interfaces between the two kinds of domains. These results bear a striking similarity with the phenomenon of an ''incubation time'' encountered in standard martensitic transformations.

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In the field of strongly correlated electrons, the family of doped manganites with general formula $R_{1-x}A_xMnO_3$ (R being a trivalent rare-earth ion and A a divalent alkaline-earth ion) is undoubtedly one of the systems that have received most attention in the recent years.[1] These materials are characterized by a particularly strong interplay between the spin, charge, orbital, and lattice degrees of freedom. This leads to remarkably complex phase diagrams, as well as various unusual properties among which the most spectacular remains the colossal magnetoresistive effect.[1] Phase-separation phenomena play a crucial role in the physics of this class of materials.[2–5]

Recently, a new and original behavior has been found in such manganites.[6–8] In some compounds of general formula $Pr_{1-x}Ca_xMn_{1-y}M_yO_3$ (with $x\sim0.5$, $y\sim0.05$, and where M is a cation used to destabilize the Mn sublattice), the virgin magnetization curves at low T display successive, abrupt steps as the field is increased. Related staircaselike behaviors were also observed in resistivity and specific-heat measurements.[6] The origin of this phenomenon is still a matter of controversy. Very different kinds of interpretation have been proposed, ranging from field-dependent orbital ordering[8,9] to a jerky growth of the ferromagnetic fraction in a phase-separation picture.[7,10] Extensive experimental investigations of this phenomenon have revealed a series of unusual features which can be regarded as key points to test the various models that have been proposed. For instance, the global pattern of steps in $M(H)$ curves was found to be affected by the value of the field spacing used in the measurement, suggesting that the average magnetic-field sweep rate plays an important role.[10]

In the present paper, we have carried out relaxation experiments in order to investigate more directly the dynamics of the magnetization jumps. We show that large magnetization steps can also be observed in relaxation experiments, i.e., in a situation where both the temperature and the magnetic field are constant. To the best of our knowledge, there have been no reports of such a steplike magnetic relaxation in any magnetic materials.

This study has been carried out on ceramic samples of two compounds for which the occurrence of magnetization steps in $M(H)$ curves is already well documented:[6,10] $Pr_{0.5}Ca_{0.5}Mn_{0.97}Ga_{0.03}O_3$ and $Pr_{0.5}Ca_{0.5}Mn_{0.95}Ga_{0.05}O_3$, hereafter denoted as [PrCa50]Ga3% and [PrCa50]Ga5%, respectively. Mn-site substitutions are known to be very efficient in destabilizing the strongly charge and orbitally ordered, CE-type antiferromagnetic ground state (AFCOO) of the parent compound, $Pr_{0.5}Ca_{0.5}MnO_3$.[11] In these Ga-substituted compounds, electron microscopy ($T=92$ K) clearly demonstrated the persistence of orbital ordering. This ordering, however, is found to be short range and inhomogeneous (there exists a distribution in the modulation wave vector around $q\sim0.4$). A neutron-diffraction study ($T=10$ K) on [PrCa50]Ga3% showed the coexistence of two magnetic phases in the zero-field-cooled ground state: a CE-type AF phase, reminiscent of the ground state of the unsubstituted compound, and a pseudo-CE-type antiferromagnetic (AF) phase like that found in $Pr_{1-x}Ca_xMnO_3$ with $x\sim0.4$.[12] The values of the magnetic moments obtained from these measurements, however, are $\sim50\%$ lower than those expected, indicating a significant amount of magnetic disorder in this complex phase-separated structure.

The magnetic measurements were carried out using an extraction magnetometer (PPMS, quantum design). Two types of $M(H)$ curves have been recorded: (i) curves with a field spacing equal to 0.25 T and a waiting time of 60 sec before each measurement (including the measuring time, the pause at each field is about 100 sec); this standard ''short-time'' procedure is typical of that used in the previous studies on these materials,[6,7] (ii) curves with a field spacing equal to 0.1 T and a pause of 10 000 sec at each field, a period during which the magnetization is recorded versus time; this ''long-time'' procedure was carried out in order to investigate the possible influence of magnetic relaxation on the occurrence of the jumps. Both types of $M(H)$ curves were recorded at $T=5$ K after zero-field cooling. Since the magnetization steps are known to be sensitive to training effects,[7,10] it must be made clear that, for both compounds, the long-time curve was recorded after the short-time data.

Figure 1 shows this set of data in the case of [PrCa50]Ga3%. The $M(H)$ curves begin with an almost linear regime, which is consistent with the antiferromagnetic character of the ground state. The first run recorded with the

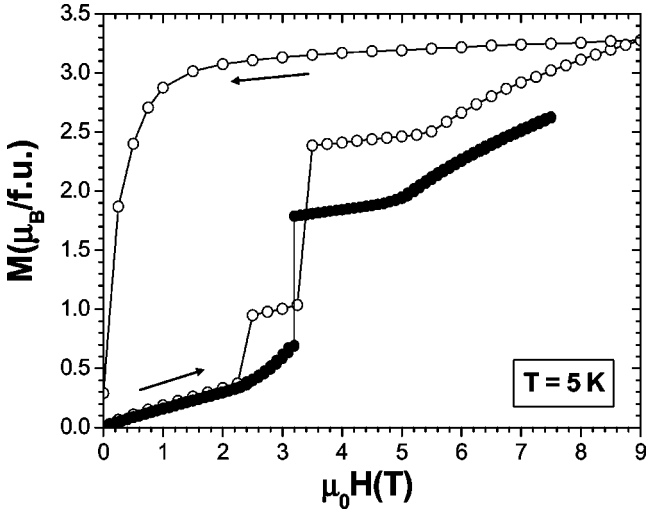

FIG. 1. Two $M(H)$ curves recorded in $Pr_{0.5}Ca_{0.5}Mn_{0.97}Ga_{0.03}O_3$ at 5 K, after a zero-field cooling. The first curve was registered with a field spacing of 0.25 T and a pause of 100 sec at each field (open circles); the second data set with a field spacing of 0.1 T and a pause of 10 000 sec at each field (solid circles). The arrows indicate the directions of field variation. Because of time constraints, the ''long-time'' $M(H)$ curve has only been recorded up to 7.5 T.

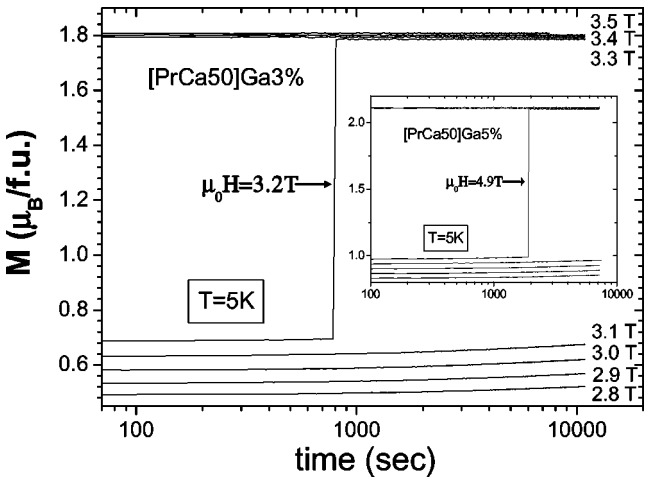

FIG. 2. Curves of magnetization as a function of time recorded in different fields for $Pr_{0.5}Ca_{0.5}Mn_{0.97}Ga_{0.03}O_3$ (main panel) and $Pr_{0.5}Ca_{0.5}Mn_{0.95}Ga_{0.05}O_3$ (inset), at $T=5$ K. The main panel shows the curves for eight magnetic fields spaced by 0.1 T in the range 2.8–3.5 T (see labels on the right); similarly, the inset shows the curves for seven fields spaced by 0.1 T in the range 4.5–5.1 T.

0.25 T field increments contains two abrupt magnetization jumps followed by plateaux, before smoothly tending to saturation ($\sim 3.4\ \mu_B$/f.u.). The reverse leg has no steps, and clearly displays the irreversible nature of the field-induced transformation. It must be emphasized that many of the differences observed between the two curves are simply related to training effects and the influence of the field spacing.[10] For instance, the smaller magnetization values found in the second run (especially in high fields) is a phenomenon typical of the training effect, and is also observed when measuring a sample twice under exactly the same conditions.[7,10] It was also shown that using smaller field increments we can delay the occurrence of the magnetization steps and modify the global shape of the $M(H)$ curve.[10] This field-spacing effect must play an important role in the occurrence of only one jump in the second run (small field spacing), taking place at a field larger than the first step in the first run (large field spacing).

Although most of the differences between the short-time and long-time experiments can be accounted for by previously identified phenomena, a closer examination of the long-time curve reveals novel behavior. In this run, we note that the magnetization jump starts and is completed at a fixed value of the applied magnetic field (3.2 T). Figure 2 displays the curves of magnetization versus time that were recorded in a range of magnetic fields around 3.2 T. The inset shows similar data for [PrCa50]Ga5%. In both cases, there is a field value at which a spectacular magnetization jump occurs when measuring as a function of time. To the best of our knowledge, such a stepwise relaxation curve has never been reported for any other magnetic material. One should note that jumps in the time dependence of resistivity have been observed in manganites—related to percolation effects—but they are accompanied by a smooth, continuous evolution of the magnetization versus time.[13] *The crucial point in the present data is the fact that this class of manganites can display a spontaneous jump in magnetization where both the temperature and the field are constant.* The existence of similar behavior for two Mn-site substituted compounds (Fig. 2) indicates that this must be a general phenomenon in this class of manganites. The data for [PrCa50]Ga5% also shows that the magnetization jump in the relaxation curve can take place after a very long time ($\sim$2000 sec). We have checked the quality of the temperature stabilization over the duration of the relaxation experiments (5.000 ± 0.004 K). One can also expect the magnetic field to be very stable for times as long as 2000 sec (the field is applied by a superconducting coil in the persistent mode). It must be noted that, unfortunately, the pronounced training effects taking place in these manganites practically rule out a reliable investigation of the reproducibility of the characteristic time of the jump, in order to assess the deterministic or stochastic nature of these instabilities.

Figure 3 shows an enlargement of the relaxation curve obtained in 3.2 T for [PrCa50]Ga3%. One can see that the magnetization jump takes place over a time interval smaller than the separation between two consecutive points, i.e., $\sim$30 sec. Figure 4 shows the same set of data as in Fig. 2 (with additional data for lower fields) is but plotted as M/M_0 versus time, where M_0 is the first measurement recorded at $t \sim 0$ for each field. One can see that the magnetic relaxation in fields larger than 3.2 T (i.e., above the jump) actually yields flat curves without detectable time dependence. In contrast, the curves in fields lower than 3.2 T exhibit a weak but sizable time dependence. In this field range, the curves can be fitted by a simple relaxation law of the form $M(H,T) = M_0(H) + [M_\infty(H) - M_0(H)]\{1 - \exp[-t/\tau(H)]\}$. Within the field range of Fig. 4, the relaxation time τ is in between 7100 and 5600 sec, decreasing as the field is increased, while M_0 and M_∞ increase with the field. Figure 4

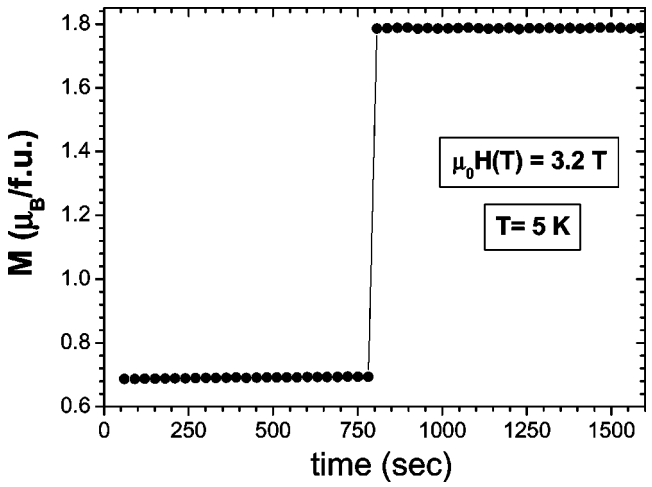

FIG. 3. Enlargement of the relaxation curve of $Pr_{0.5}Ca_{0.5}Mn_{0.97}Ga_{0.03}O_3$ showing a jump for fixed values of the temperature (5 K) and of the magnetic field (3.2 T).

shows that the normalized relaxation curves are progressively shifted upward as the field is increased in the range 2.5–2.9 T. For higher fields, there seems to be a saturation effect with the last three curves (2.9–3.1 T) superimposed on each other. More generally, the behavior at 3.2 T is reminiscent of an *explosive instability*, where the response of the system (in this case, the magnetization) goes to infinity at a finite time. A generic example of such an instability arising from a three-wave interaction is discussed in some detail in Ref. 14.

The stepwise magnetic relaxation reported here sheds new light on the phenomenon of magnetization jumps observed in Mn-site substituted manganites. In particular, the occurrence of such a jump in a constant field shows that this phenomenon is not solely driven by a change in the magnetic energy term. It thus brings into question the relevance of interpretations based on the concept of critical fields to account for the

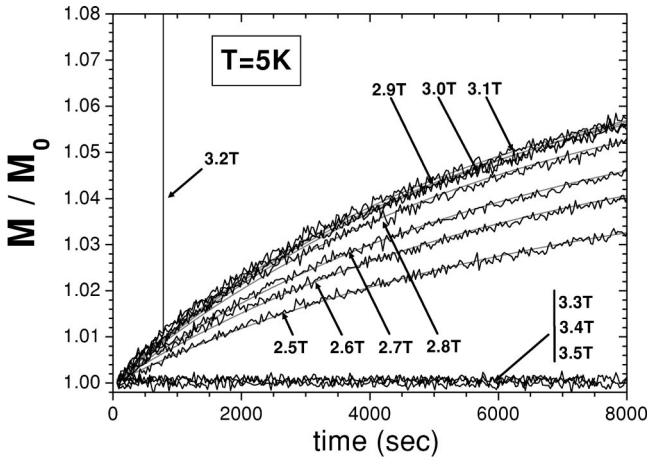

FIG. 4. Relative variation of the magnetization of $Pr_{0.5}Ca_{0.5}Mn_{0.97}Ga_{0.03}O_3$ as a function of the time (M_0 is the first measurement at $t \sim 0$), in a range of fields from 2.5 to 3.5 T, at $T = 5$ K. Thick gray lines are fitting curves (see text) for the field values up to 3.1 T.

magnetization steps in $M(H)$ curves.[8] Moreover, we show in detail below that these new results turn out to be qualitatively consistent with the previously proposed ''martensitic'' scenario, in which the steps correspond to a burstlike growth of the ferromagnetic component in the phase separation.[10]

The martensitic character of some phase transformations in manganites has been previously emphasized by Littlewood,[4] as well as Uehara and Cheong.[5] This is due to the fact that manganites can exhibit transitions (induced by temperature and/or field) between magnetoelectronic phases having very different unit cells. In manganites, some antiferromagnetic phases exhibit pronounced structural distortions because of a concomitant long-range ordering of the Mn^{3+} e_g orbitals. In the case of the CE-type antiferromagnetic phase, a checkerboardlike ordering of the d_{z^2} orbitals produces a large distortion of the perovskite cell.[12] The setting of this AFCOO state is favored in half-doped compounds with small cations such as Pr or Ca at the perovskite *A* site. In such compounds, one thus faces a remarkable situation where the unit cell[15] of the antiferromagnetic phase is very different in shape from those of the paramagnetic (P) and ferromagnetic (F) phases. Martensitic features have been previously attributed to temperature-induced P/AFCOO and AFCOO/F transitions.[5,16,17] Recently, we have proposed that the steps in $M(H)$ curves could be related to the martensitic nature of the field-induced AFCOO/F transformation.[10] Various observations accompanying this phenomenon (such as the training effect and the influence of the field spacing, i.e., the rate of variation of the driving force) were found to be consistent with the behavior encountered in martensitic transformations.[18]

Remarkably, the stepwise magnetic relaxation presented here can also be related to peculiar behavior found in standard martensitic transformations. For instance, in Fe-31.7-at %Ni, Kakeshita *et al.*[19] reported a curve of resistivity versus time that is strikingly similar to Fig. 4, i.e., an abrupt jump at $t \sim 1000$ sec separating two plateaus. In this experiment, the sample was held at a fixed temperature slightly above the ''martensitic start'' temperature, and the development of the transformation was monitored via the resistivity. Here, the sample is kept in a magnetic field close to the metamagnetic transition and magnetization measurements are used to track the transformation. The existence of a silent time before the start of the transition in the so-called *isothermal* martensitic transformations is known as the ''incubation time'' effect.[20] In the present data, it must be noted that the magnetization was found to vary slightly in the time interval preceding the jump, by about 1.2% and 1.8% for [PrCa50]Ga3% and [PrCa50]Ga5%, respectively. Remarkably, the same kind of exponential time dependence has been recently reported for the evolution of the magnetic-field-induced strains in martensitic Ni-Mn-Ga alloys.[21]

To summarize, an unusual stepwise magnetic relaxation has been found in Mn-site substituted manganites. At constant temperature and field, a large magnetization jump (of the order of one-third of the full spin polarization) can take place after a long incubation time (of the order of 1000 sec). This result is consistent with a previous interpretation of the

magnetization jumps in $M(H)$ curves, in terms of burstlike growths of the ferromagnetic fraction in these phase-separated systems.[10] This peculiar relaxation effect is also found to lend further support for the existence of a close analogy between the metamagnetic transition in Mn-site substituted manganites and the isothermal martensitic transformation in metallic alloys. Finally, we note that the manganites—in addition to all their unusual properties—may also be well suited as candidates for the investigation of *explosive instability* phenomena in solid-state physics.

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