Superspin glass behavior of a nonstoichiometric lanthanum manganite $LaMnO_{3.13}$

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Aging and memory effects are observed in an oxygen nonstoichiometric lanthanum manganite $LaMnO_{3.13}$ from time-dependent dc magnetic measurements by employing various cooling protocols. The results can be best described by the superspin glass model of interacting magnetic nanoparticles system. The possible origin of such a behavior is the confinement of interacting small magnetic clusters formed as a result of the formation of manganese vacancies, along with the random distribution of tetravalent manganese ions in the lattice.

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$LaMnO_3$ in which Mn is present as the high-spin $Mn^{3+}(S=2)$ is an antiferromagnetic oxide.[1] The material can be made ferromagnetic by the introduction of Mn^{4+} ions in the lattice of $LaMn^{3+}O_3$ and this is due to the double exchange mechanism involving manganese ions in 3+ and 4+ oxidation states and mediated by the linking oxygen. The introduction of cationic vacancies by forcing excess oxygen nonstoichiometry as in $LaMnO_{3+\delta}$ or as $La_{1-x}MnO_3$ (self-doping) incorporates Mn^{4+} in $LaMnO_3$, apart from the substitution of La^{3+} by divalent ions. The value of δ in $LaMnO_{3+\delta}$ plays an important role in determining the structure and the magnetic properties. As the perovskite structure of $LaMnO_3$ is a close-packed structure, it is not possible to accommodate excess oxygen in the lattice and hence cation deficient models such as $La_{1-x}Mn_{1-x}O_3$ and $La_{1-x}Mn_{1-y}O_3$ have been proposed.[2–4] The self-doped compositions at low doping levels are more Mn deficient $(y>x)$.[5] The cation deficiencies at both the La and Mn sites, along with the large amount of Mn^{4+}, can have serious effects on the magnetic properties of $LaMnO_{3+\delta}$. In fact, spin glass (SG) nature is reported for $LaMnO_{3.15}$, though no antiferromagnetic contribution is detected from neutron-diffraction studies.[2]

Recent studies on time dependence of magnetization of magnetic nanoparticles suggest that each particle could be considered as having a single spin (superspin) and interactions between them cause frustration, resulting in superspin glass (SSG) behavior, whereas the noninteracting superspins give rise to superparamagnetic (SPM) behavior.[6] The SSG and SPM systems show slow dynamics and, in the former case, it is caused by frustration and strong dipolar interactions among the particles, whereas broad distribution of the relaxation times is responsible in the latter. The frustrated superspin glasses and superparamagnets deviate from the equilibrium behavior below the freezing or glass-transition temperature (T_f) and show complex time dependence of magnetic properties. These complex dynamic properties, especially the waiting time dependence on the magnetization under different cooling protocols, have been observed in various materials.[7,8] The logarithmic response of the magnetization on the time spent at temperatures lower than the T_f—the aging effect—and the retrieval of this magnetic state at a given temperature after a negative temperature cycle—the memory effect—have been a field of great interest in the area of condensed matter physics in the recent past.[9,10] The observed physical properties suggested the possibilities of having a hierarchical organization of metastable systems in which new states are derived from the old as temperature is lowered and then reformed on heating.[7,11] The droplet model that considers the logarithmically slow domain growth at a given temperature with time is suggested to explain such behavior in various systems.[11–13]

In this paper, we show that a nonstoichiometric lanthanum manganite $LaMnO_{3.13}$ can be best described as a SSG system of small and interacting magnetic clusters, as evidenced from time-dependent dc magnetic measurements. Polycrystalline $LaMnO_{3.13}$ was prepared by the solid state method as reported elsewhere.[4] The structure of the final composition was found to be rhombohedral from the powder x-ray diffraction analysis and the amount of Mn^{4+} was determined by standard redox titration methods. The dc magnetization studies under various protocols were performed using an EG&G PAR vibrating sample magnetometer from 12 to 300 K.

Thermomagnetic irreversibility between zero field cooled magnetization (ZFCM) and field cooled magnetization (FCM) is a well-known characteristic of spin glasses and superparamagnetic nanoparticles.[6,11,14] Figure 1 shows the zero field cooled (ZFC) and field cooled (FC) behavior of $LaMnO_{3.13}$ measured in two different magnetic fields. In all measurements, the cooling and the warming rates were kept

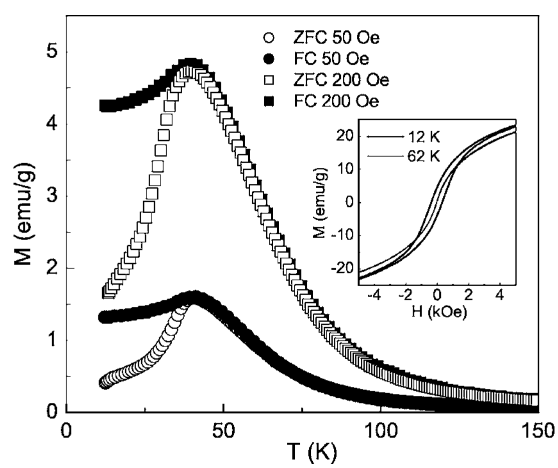

FIG. 1. ZFC and FC magnetization curves of $LaMnO_{3.13}$ at two different fields, 50 Oe and 200 Oe. Inset: M versus H curves at 12 K and 62 K.

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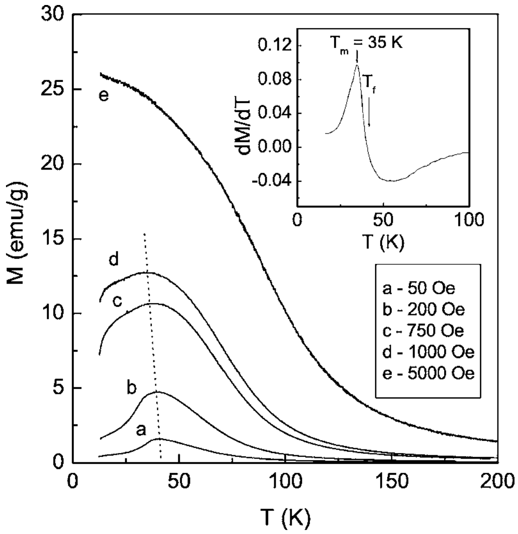

FIG. 2. Field dependence of the ZFC magnetization of $LaMnO_{3.13}$. The dotted line is a guide to the eye. Inset: Derivative of the ZFCM curve at 50 Oe, as a function of temperature.

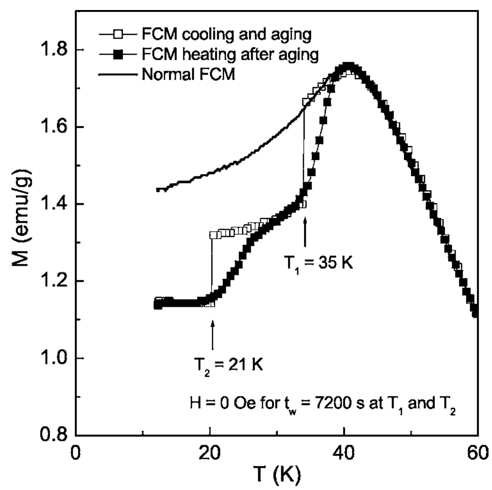

FIG. 3. *M-T* measurement during cooling under a field of 50 Oe. During cooling, the field was switched off at two temperatures T_1 and T_2 for a waiting time, t_w=7200 s (open squares). The *M-T* measurement was repeated in the heating mode (filled squares). The normal FCM curve (solid line) is shown for comparison.

identical, without any waiting time during the temperature sweep. A cusp is observed in the ZFCM curve at 41 K in a field of H=50 Oe and this is identified as the freezing temperature (T_f), as observed in conventional spin glasses and superparamagnets. The FCM curve also shows a less pronounced cusp but with definite irreversible behavior below T_f with respect to the ZFCM data. Magnetic hysteresis is observed at all temperatures below T_f whereas no hysteresis is observed above T_f, as shown in the inset of Fig. 1. No significant difference in the magnetic irreversibility behavior is observed when H is increased from 50 to 200 Oe, except that T_f is slightly shifted to a lower temperature of 40 K. In order to see the dependence of T_f on the applied field strength, ZFCM-T measurements have been performed at various field strengths, as shown in Fig. 2. T_f is shifted to lower temperatures as H is increased, with increased broadening of the cusp and finally the cusp disappears when H =5 kOe. This clearly shows the aid of activation energy required for the low temperature state to attain equilibrium either in the form of magnetic field or thermal energy. The inset of Fig. 2 shows the derivative of the ZFCM curve measured at 50 Oe, which shows that maximum change in the magnetization below T_f takes place in a narrow temperature region centered at 35 K. The derivative of the FCM curve also showed a similar feature.

The magnetic hysteresis behavior below T_f and the shifting of the cusp to lower temperatures associated with broadening at higher fields are typical characteristics of a SPM system. The similarity between the magnetic behavior of the manganite sample under investigation and conventional superparamagnets suggests the existence of magnetic clusters in the former, which could be approximated as superspins individually having nanodimensions. An adequate explanation for the formation of small superspin clusters would be the nanoscale phase separation in $LaMnO_{3.13}$ produced due to at least two important factors: the probable Mn vacancies and the inhomogeneous distribution of large amounts of Mn^{4+} ions. Assuming equal La and Mn vacancies in the structure, then the composition of $LaMnO_{3.13}$ corresponds to $La_{0.96}Mn_{0.96}O_3$, indicating 4% Mn vacancies in the structure. On the other hand, assuming that there are no La vacancies in the lattice, the Mn vacancies would be approximately 8%. The actual value can be within the limits of 4% and 8%. These kinds of Mn vacancies restrict the long-range ordering of the double exchange clusters and localize them as if they are embedded in a nonmagnetic matrix. Ritter *et al.* found a similar cusp in the ZFCM curve of $LaMnO_{3.15}$ below 50 K and suggested the existence of a disordered cluster glass state in the system.[2] The conclusions are based on equal La and Mn vacancies and findings from neutron diffraction and SANS studies where no long-range order is observed down to lowest temperatures. The magnetic correlation length is obtained as 15–20 Å, from magnetic SANS intensity data, which represents the average sizes of the magnetic clusters. An immediate question that arises is whether such small superspin clusters are interacting or isolated. In other words, whether the system is an interacting superspin glass or an ideal noninteracting superparamagnet. The behavior of the FCM curve below T_f is a primary indication for the SSG nature, as per the convention of Sasaki *et al.*[6]

In order to understand the interacting and/or noninteracting behavior of the superspins, time-dependent magnetization studies under various cooling and heating protocols have been performed. The first one is a double memory experiment (DME) under FC protocol. In a DME, a typical SSG or SPM system shows aging, rejuvenation, and memory effects.[6] The DME results are shown in Fig. 3 along with the FCM curve for reference. A constant field of 50 Oe was applied during all these measurements. The results clearly show the decay of magnetization (aging effect) at two well-defined temperatures T_1=35 K, where maximum change in ZFCM and FCM is observed below T_f (T_m in Fig. 2) and T_2=20 K, where the magnetic field was reduced to zero and again increased to 50 Oe after a waiting time of t_w=7200 s

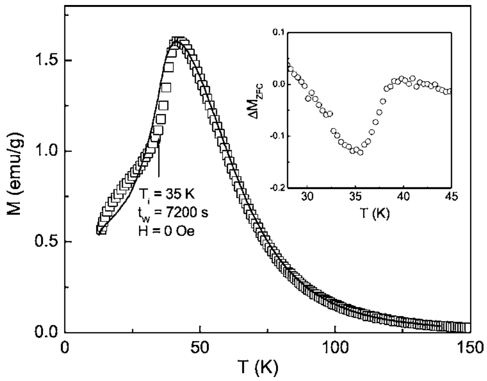

FIG. 4. ZFCM curve recorded after a waiting time of t_w $=7200$ s at 35 K during ZFC process (symbols). The normal ZFCM curve (solid line) is shown for comparison. Inset: The difference between the aged and normal ZFC magnetization (ΔM_{ZFC}) as a function of temperature.

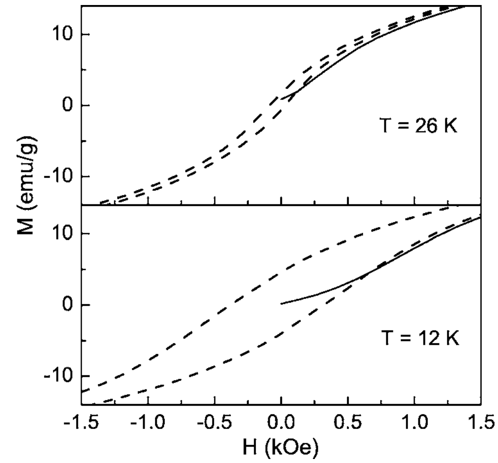

FIG. 5. The initial magnetization curves (solid lines) and hysteresis loops (dotted lines) showing the strong irreversibility of the magnetization process at low field strengths.

when measurement was performed during field cooling. After cooling to the lowest temperature, the magnetization is measured while warming without any intermittent stops. As shown in Fig. 3 (filled squares), it is found that the system remembers its thermal history or the magnetic state reached by the system during the cooling cycle. Such a memory effect implies that the metastable configuration formed at lower temperatures (say, T_2) does not have any influence on the configuration formed at a higher temperature. Such memory effects are usually observed in interacting magnetic nanoparticles attributed to the SSG behavior and explained using the hierarchical organization scenario,[15] as well as for superparamagnets and random field systems.[6,9] This makes it complicated to distinguish the glassy behavior from the above-mentioned systems from the DME alone.

Another protocol has been suggested to confirm whether the memory effect observed is due to the SSG behavior or not, wherein an intermittent stop for a period of time is performed during the ZFC process at a particular temperature during cooling under zero field.[6,16,17] The ZFC measurement is performed as usual after cooling to the lowest temperature while heating in an applied field of 50 Oe. The results of such a single memory experiment (SME) followed by the above protocol is compared with the standard ZFCM curve in Fig. 4. The temperature was kept constant at 35 K for a period of $t_w=7200$ s while cooling. There is a clear memory effect, as indicated by the cusp at $T_i=35$ K in the difference curve shown in the inset of Fig. 4. In a typical SSG, during the intermittent stop, the spin correlation length of SG order increases and this is reflected ultimately upon heating as the memory effect. This is not expected in the case of noninteracting nanoparticle systems.[6]

In addition to the above characteristics, another interesting feature exhibited by the manganite system is the nature of the magnetization curves. As mentioned, well-defined magnetic hysteresis loops are obtained below T_f. However, the initial magnetization or the virgin curve at higher magnetic fields is found to lie outside the hysteresis loop above a certain field, as shown in Fig. 5. The virgin curve intersects with the hysteresis loop at a field larger than the coercive field H_c, and this behavior is observed at all temperatures below T_f with the difference between the field of intersection H_i and H_c increasing with decreasing temperature. In fact H_i is almost double that of H_c. The virgin curve overlaps with the hysteresis curve only at high magnetic fields. This behavior is quite uncommon and has been observed in some dilute alloy systems such as $Au_{81}Fe_{19}$,[18] as well as in a ferrimagnetic oxide $MnCo_2O_4$.[19] The characteristics of the virgin curve of a magnetic material, in general, reflect the pinning nature of the domains. The fact that the virgin curve lies outside the loop is indicative of some irreversible pinning-depinning effects.

Thus, the manganite sample $LaMnO_{3.13}$ can be thought to be constituted by single domain clusters with short-range magnetic ordering, which are separated, but still interacting with each other as in the case of magnetic nanoparticles. Mn-site vacancies and inhomogeneous distribution of Mn^{4+} ions in the lattice lead to the formation of small magnetic clusters, each of them having individual superspins and corresponding relaxation times. The size of the clusters may vary depending on the distribution of the vacancy and Mn^{4+} ions in the lattice. Ritter *et al.*[2] showed from SANS studies that for $LaMnO_{3.15}$ the magnetic correlation length increases slowly below 100 K (from ~15 Å) and becomes almost constant (~18 Å) below $T_f \approx 50$ K. Hence it is possible that in the case of $LaMnO_{3.13}$, the size of the clusters increase with decreasing temperature. The interactions between the magnetic clusters formed may be of the dipolar type.[20] Another possibility is the anisotropic exchange interactions of the Dzyaloshinskii-Moriya (DM) type operating through the strongly distorted regions of Mn-site vacancies. The presence of DM interactions has been predicted,[21] and observed experimentally,[22] in distorted lanthanum manganite.

A more realistic scenario to explain the observed magnetic behavior would be a droplet picture, where the aging corresponds to the gradual change of the superspin interactions. The simplest picture would be the pinning mechanism, which separates the droplets formed by the interaction of superspins from one another and as field or temperature increases, the unpinning occurs. The Mn-site vacancies and/or inhomogeneous distribution of Mn^{4+} ions may act as the

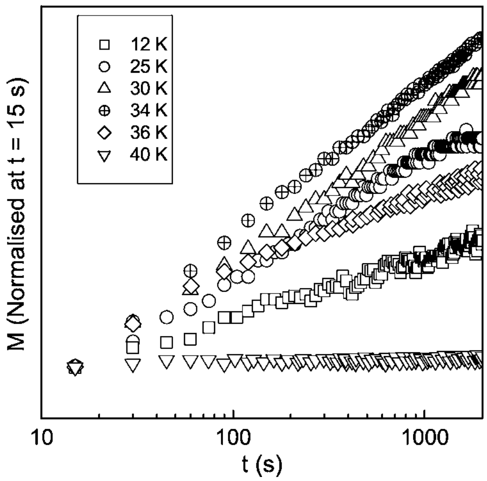

FIG. 6. Time dependence of the ZFC magnetization in a field of 50 Oe at different temperatures.

droplet pinning centers. Such a pinning model can be found to be consistent with temperature dependent relaxation behavior, as shown in Fig. 6 where the relaxation is studied under ZFC protocol. The largest change in the magnetization with time is observed at the temperature where there is a large drop in the ZFC magnetization (see inset of Fig. 2), indicating the possibility of a narrow distribution of the relaxation times. In addition, the strong irreversibility of initial magnetization also manifests the pinning-depinning mechanism involved in the superspin dynamics below T_f.

In the aging experiment under the FC protocol with a small applied field, larger droplets are formed just below T_f and during the stop at T_1, the system relaxes faster (less pinning at high T) as shown by the fall at T_1 in the aging curve in Fig. 3. Further field cooling process does not affect this metastable equilibrium (or completely pinned superspin) formed after aging under a reasonably larger cooling rate (relative to the rate at which the equilibrium is attained) and new smaller droplets are formed below T_1 (more pinning at low T). Once the field is on, the magnetic state formed after aging at T_1 requires an indefinitely long time to relax back to the original state before aging. Since the system is continuously cooled below T_1, the superspin may tend to go back to the state at T_1 but never reaching it due to the imprinted irreversible pinning effects and/or thermal blocking. As temperature decreases, aid from thermal energy for the unpinning process is reduced. When the temperature is T_2 ($T_2 < T_1 < T_f$), the sample is again aged and the same reversible and irreversible processes occur at this lower temperature. Thus, in a typical DME we have two types of pinned droplets formed at T_1 and T_2, the formations of which are totally independent. On the reverse thermal cycle, under the same applied field, the same magnetic behavior as in the FC mode is expected up to T_2, and at T_2, the imprinted metastable state which is a strongly pinned droplet, is remembered (the pinned states are activated due to the availability of sufficient thermal energy) during the measurement. As temperature is further increased, normal unpinning of the droplets results until the system reaches T_1. At T_1, the completely pinned metastable state is again remembered. Thus, the simple pinning and depinning processes of droplets formed by the interaction of superspins qualitatively explain the observed aging and memory effects in $LaMnO_{3.13}$. For an interacting nanoparticle system, the FC magnetization remains almost constant below T_f.[6] In the present case, the FC magnetization slightly drops below T_f and decreases further. This is likely to be an indication for stronger pinning effects and interactions among the small magnetic clusters. In conclusion, the present study shows that magnetic behavior of $LaMnO_{3.13}$ can be described by the superspin glass model of interacting nanosized magnetic clusters.

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