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Magnetocaloric effect of polycrystalline $Sm_{0.5}Ca_{0.5}MnO_3$ compound: Investigation of low temperature magnetic state

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ABSTRACT

An attempt has been made to probe low temperature magnetic state of the polycrystalline $Sm_{0.5}Ca_{0.5}MnO_3$ compound via magnetization and magnetocaloric studies. In the context of the earlier debatable reports on the above mentioned compound between the existence of glassy magnetic state and small ferromagnetic domains from the 'ac' susceptibility measurements, our experimental observation from magnetocaloric effect study clearly indicates the existence of ferromagnetic droplets along with certain amount of superparamagnetic component at low temperature (< 40 K) which begins at T ~ 100 K. In addition to that, the zero field cooled magnetization (even at H = 0.01 T) data do not exhibit the spin freezing nature at the low temperature which is almost a generic tendency of glassy magnetic state. Our study also highlights the competence of magnetocaloric effect as a tool to distinguish between different magnetic states of a compound.

1. Introduction

An extensive effort has been made in the last two decades to study the physical properties of doped perovskite manganites having general formula $R_{1-x}D_xMnO_3$ (R = trivalent elements, D = divalent elements) [1–21]. Depending upon the A-site ionic radius ($R_{1-x}D_x$), manganite compounds exhibit different appealing properties. In un-doped manganites, generally antiferromagnetic ground state is observed. Doped perovskite manganites received utmost attention due to the observation of colossal magnetoresistence (CMR), charge ordering (CO), phase separation, ferromagnetism *etc.*. Charge ordering is the real space ordering of the Mn^{3+} and Mn^{4+} ions in the crystal and it is almost a generic property of the doped manganites. Charge order compound is generally accompanied with an antiferromagnetic (insulating) ground state at low temperature. The insulating antiferromagnetic ground state can be transformed into the metallic state by application of external magnetic field, electric field, x-ray irradiation *etc.*. On the other hand there are many reports about the phase separation where the co-existence of the ferromagnetic metallic and charge ordered insulating phases coexist. Such kind of the phase separation in manganite system has finite effect in its physical properties namely in magneto-transport and magnetic properties. Electronic phase separation also play an important role for the large negative magnetoresistance mediated by the transforming of the charge ordered insulating phase to ferromagnetic metallic phase in the presence of external magnetic field. For technological aspects, large magnetoresistance and large magnetocaloric effect in highly chemically stable ferromagnetic doped manganites and less robust charge ordered manganites (and their nanomaterials) have been extensively studied [5,22,23]. In contrast to that, a less effort is made to study robust charge ordered manganites namely $Ln_{0.5}Ca_{0.5}MnO_3$ (Ln = Gd, Dy, Sm *etc.*). In case of the robust charge ordered systems, a very high magnetic field is required to destabilize the insulating ground state for achieving the significant magnetoresistance. However, it is worth mentioning that from fundamental aspects, several intriguing properties of the robust charge ordered materials had been previously reported [24,25]. Specially for $Sm_{0.5}Ca_{0.5}MnO_3$ compound, the physical properties have been extensively studied for bulk as well as its nanoparticles [16,25–27].

For the bulk $Sm_{0.5}Ca_{0.5}MnO_3$ (SCMO) compound, the previous studies indicate that to melt the charge ordered antiferromagnetic state at low temperature (~4 K) a very high magnetic field is required (~50 T) [16]. With decrease of the temperature, charge ordering of that compound was observed at T ~ 260 K and antiferromagnetic ordering appeared at T ~ 150 K[16]. Recently Giri et al. reported the proper-

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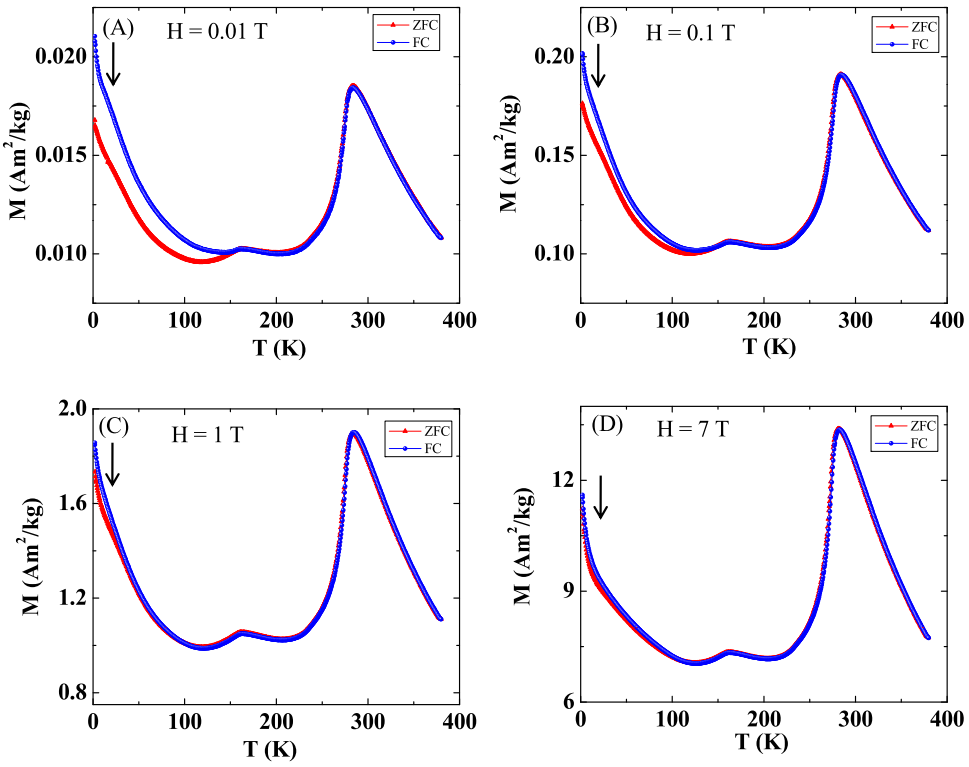

Fig. 1. Magnetization as a function of temperature at different external magnetic fields.

ties of the magnetic ground state and the exchange bias properties of nanosized as well as bulk SCMO compounds [26,27]. According to their study from 'ac' susceptibility measurements, there exists spin glass like state at low temperature region even in bulk SCMO [26,27]. In contrast to these results Xu et al. reported from magnetization and ac susceptibility measurements that in bulk SCMO compound, there is no spin glass signature at the low temperature [25]. Additionally, in their report it was mentioned that there is a possibility of existence of a ferromagnetic fraction at low temperature region [25]. Such phase coexistence (ferromagnetic droplets in antiferromagnetic matrix) in the SCMO compound at low temperature may be responsible for the exchange bias effect which was mentioned earlier (in Ref. [16]). Clearly there is a disagreement in the literature about the low temperature magnetic state of SCMO. Isothermal magnetization measurements can remove this ambiguity about the low temperature magnetic state. In general for ferromagnetic systems, in the isothermal magnetization measurements at different temperature, magnetization value decreases with increasing temperature. However in contrast to that the opposite behavior should be found in case of the glassy magnetic state *ie.* the magnetization value should increase with increasing temperature. In case of glassy systems, at low temperature region (below the spin freezing temperature) the magnetization increases with increase of temperature as the thermal energy helps to orient the moments along the field direction.

In our present study, we have investigated the low temperature magnetic state of the bulk SCMO compound via magnetization and magnetocaloric measurements. Our results clearly indicate that the magnetocaloric responses of that compound signify the existence of the ferromagnetic droplets at the low temperature (there is also the possibility of existence of a superparamagnetic component). In the present work we have shown that the study of magnetocaloric effect can distinguish between the spin glass state and the existence of ferromagnetic droplets. Such studies have removed the ambiguity of the low temperature magnetic state of SCMO.

2. Sample preparation, characterizations and measurements

Polycrystalline bulk $Sm_{0.5}Ca_{0.5}MnO_3$ compound was prepared by the standard sol-gel processes. For the sample preparation, starting elements were pre-heated Sm_2O_3, $CaCO_3$, MnO_2 and concentrated HNO_3. Additionally, oxalic acid and citric acid of appropriate amount were used to prepare the precursor solution. The details about the sample preparation method in sol-gel method was given in Ref. [28]. The sample used for the present study is the same sample which was used in Ref. [28].

For the characterization of the sample, x-ray diffraction study was carried out using Rigaku-TTRAX-III diffractometer with Cu-Kα source having wave length $\lambda = 1.54$ Å. For the study of magnetic and magnetocaloric effect, we have utilized a superconducting quantum interference device (SQUID) magnetometer (Quantum Design).

3. Results and discussion

Room temperature x-ray diffraction data analysis (profile fitting by Rietveld method) has manifested the single phase nature of the compound. The profile fitting data and the lattice parameters were previously enlisted for the same compound in Ref. [28].

Magnetization as a function of temperature in the different external magnetic fields is shown in Fig. 1. In the experimental data, the usual signature of charge ordering ($T \sim 270$ K) and antiferromagnetic ordering ($T \sim 150$ K) are clearly visible in all sets of data (measured at different magnetic field in Zero field Cooled (ZFC) and Field Cooled (FC) protocols). Another interesting observation is that, in the low temperature region, the spin freezing nature in ZFC magnetization is absent here in all the measurements (Fig. 1). Such nature of the magnetization attracts a special interest to study the physical properties and differs this compound as reported in numerous other manganite compounds [2,3]. At very low values of the external magnetic field, bifurcation is found between the ZFC and FC magnetizations. However, bifurcation is reduced for the larger values of the magnetic field. Another important

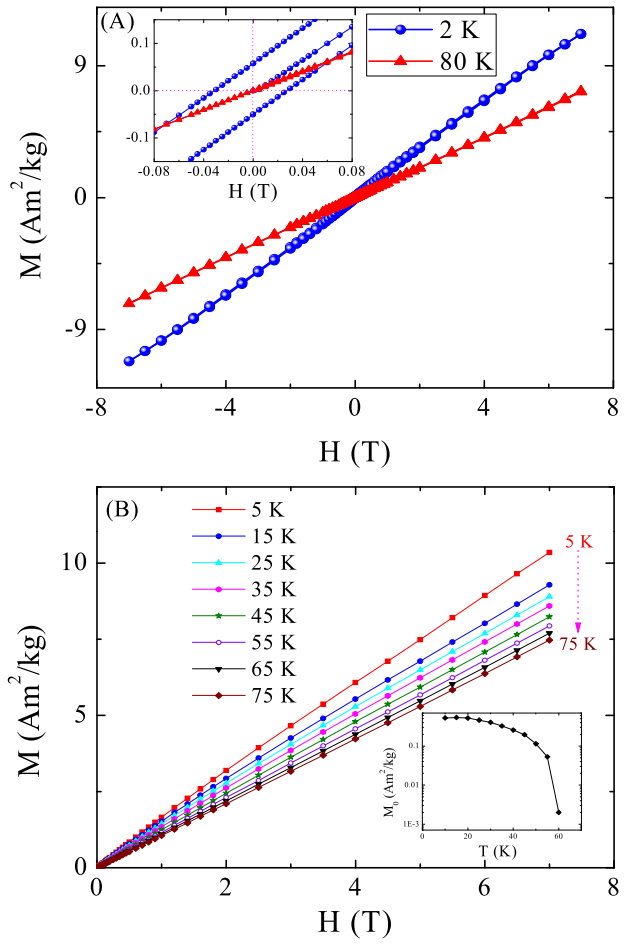

Fig. 2. (A) Magnetization as a function of external magnetic field at T = 2 K and 80 K temperature. Upper inset shows the enlarged view of the magnetization at low field region. (B) Magnetization as a function of external magnetic field at different specified temperature of $Sm_{0.5}Ca_{0.5}MnO_3$ compound at low temperature region. (Lines are guide to the eye.). Lower inset is the temperature dependence of sponteneous magnetization.

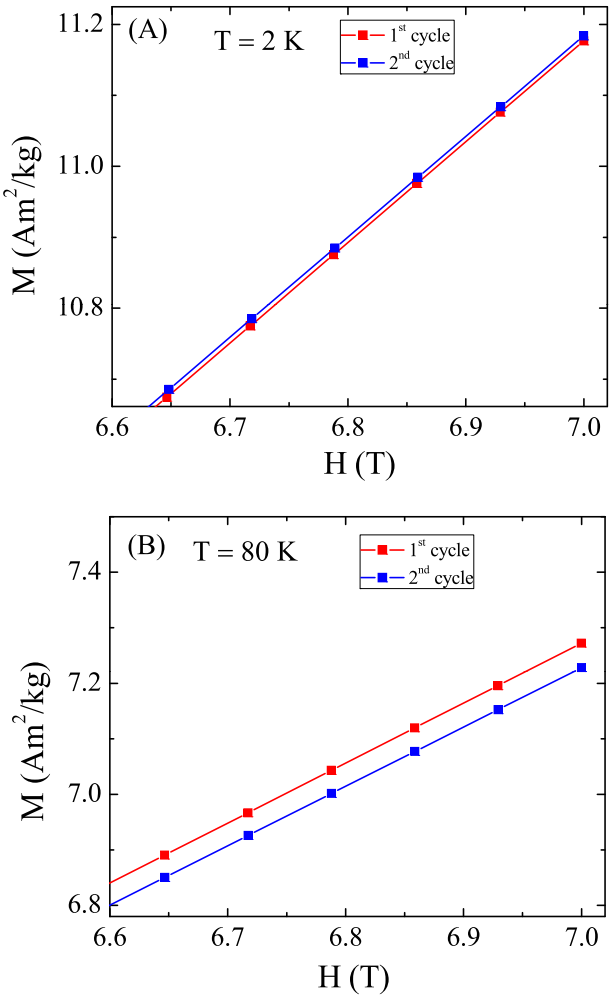

Fig. 4. (A) and (B) indicate the enlarged view of the magnetization at T = 2 K and 80 K in the 1^{st} quadrant in 1^{st} and 2^{nd} cycle (5^{th} quadrant) respectively.

aspect here is that below T = 100 K, a sharp increase of non-saturating magnetization is observed (in both ZFC and FC). Generally, for super-

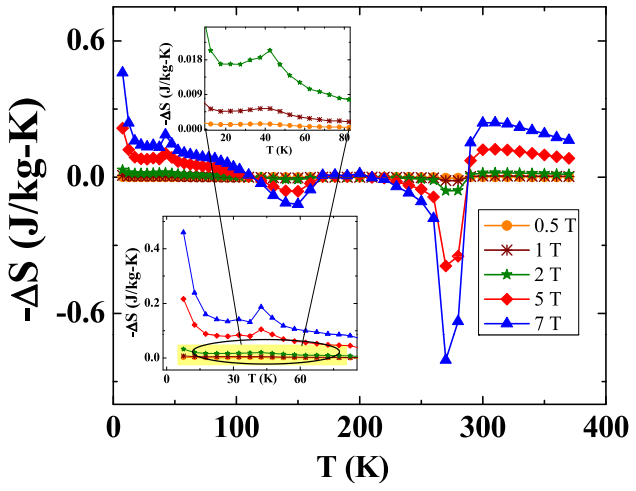

Fig. 3. Magnetocaloric entropy change of the $Sm_{0.5}Ca_{0.5}MnO_3$ compound as a function of temperature at different magnetic fields. The insets show the enlarged views of the low temperature region to reveal the presence of the inflection point at high field (lower inset) and at low field regions (upper inset) as indicated by the oval at the lower inset.

paramagnetic systems the relation $M \sim T^{-1}$ is followed (as indicated in Fig. 1 by arrows). But, in the present case, upon careful observation of the magnetization data one can easily find out that the magnetization does not follow such temperature dependence. Another important aspect is that in case of manganites, the spin freezing (blocking in ZFC magnetization) is almost a common trend [7]. But in our present study such behavior was not observed. Hence it may be assumed that in our present study such increasing nature of the magnetization at lower temperature region cannot be explained by considering superparamagnetism alone. One important fact should also be mentioned here which is the effect of the rare-earth ions ordering in the magnetization of doped perovskite manganites. According to the reported study by Lopez et al., in case of the $Sm_{0.5}Ca_{0.5}MnO_3$ compound, the similar kind of increasing nature of the magnetization was observed at low temperature [29]. They have also pointed out that there was no long range ordering between the Sm^{3+} ions even at the lowest measured temperature [29]. Such increasing magnetizations at low temperature may be inferred as a formation of substantial ferromagnetic counterparts (droplets) along with super paramagnetic nanoclusters (a small fraction) in the antiferromagnetic matrix of robust charge ordered $Sm_{0.5}Ca_{0.5}MnO_3$ compound. At very low temperature (T ~ 40 K), the rate of increase of magnetization for ZFC is smaller than for FC. This is a possible ndication of blocking of superparamagnetic (SPM) clusters which should provide smaller magnetization value below this temperature (T ~ 40 K). However this response superposed on the

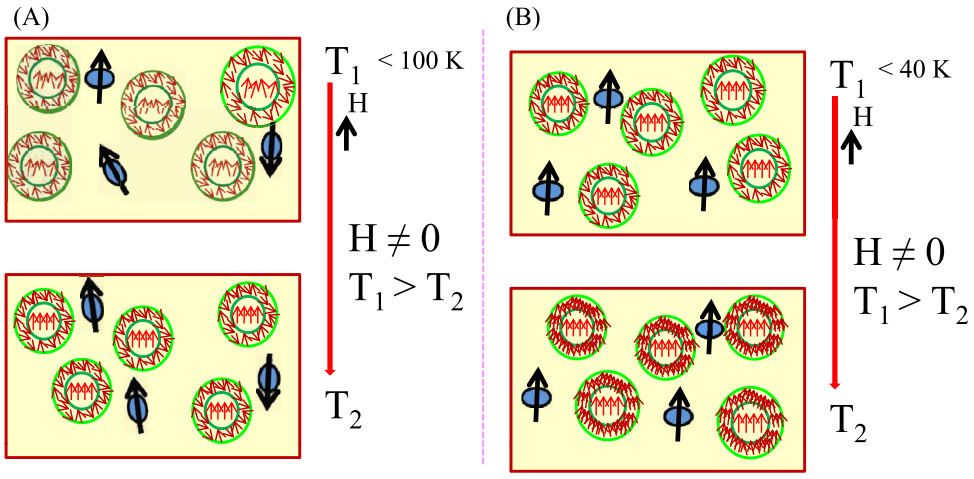

Fig. 5. Schematic representations of the existence of ferromagnetic droplets within the antiferromagnetic background at the low temperature region. Black ovals indicate SPM clusters in the AFM matrix (black arrow indicates super spin of the whole cluster).

increasing ferromagnetic contribution. That is why the usual magnetic response of a SPM system below T_B (Blocking temperature) is not clear here.

For a better understanding of the nature of magnetization at low temperature, we have carried out isothermal magnetic measurements (M-H) at T = 2 K and 80 K. The magnetization *vs.* external magnetic field data are shown in Fig. 2(A). At both the temperatures, the magnetization shows almost a linear dependence on filed, a reflection of the predominant antiferromagnetic background of the sample. However, a detailed observation in the low field region (shown in upper inset of Fig. 2(A)), a prominent hysteresis loop at the low temperature (T = 2 K) is seen with a significant coercive field (H_C ~ 0.04 T). Generally for the superparamagnetic state for the nanoclusters, the coercive field as well as magnetic hysteresis is very small. From this basis the significantly larger coercive field may be associated with the presence of a ferromagnetic phase fraction, ordered at low temperature. At T = 80 K, the magnetic isotherms exhibit liner behavior, analogous to response of the antiferromagnetic compounds as earlier. But, at the low field region there is no signature of the magnetic irreversibility (upper inset of Fig. 2(A)). As mentioned earlier, though the sharper increases of magnetization was observed below T = 100 K in the M-T data (Fig. 1), the hysteresis loop disappears above T ~ 60 K. We have recorded the magnetic isotherms at different temperatures. These M-H data are shown in Fig. 2(B). We have extracted the spontaneous magnetization (M_0) by extrapolating the liner fitting to the magnetization data (M(H)) at the higher magnetic field region (H > 4 T). Temperature dependent spontaneous magnetization is given in the lower inset of Fig. 2(A) which indicates that the M_0 sharply decreases above T ~ 50 K.

The overall indication of the magnetic measurements and the discussion in the earlier part elucidate that at the low temperature region, sol-gel prepared polycrystalline bulk $Sm_{0.5}Ca_{0.5}MnO_3$ compound exhibits quite different nature than the glassy behavior which is in agreement with the earlier report [25]. Hence, sharper increasing nature of the magnetization with decrease of temperature at low temperatures may be ascribed to the formation of the small fraction of the ferromagnetic droplets within the antiferromagnetic background. Regarding this argument, it is obvious to mention that in antiferromagnetic systems, below the transition temperature (Neel temperature, T_N), magnetization value increases with increasing temperature. While the opposite nature appears in ferromagnetic systems in general (saturation value decreases with increasing temperature). In case of the $Sm_{0.5}Ca_{0.5}MnO_3$ compound it is reported that charge ordered antiferromagnetic state is very much robust (endorse the small magnetization value) [16]. In our present study, we have measured magnetic isotherms at several fixed temperatures. Before starting any measurements, first the sample was cooled down from well above to its paramagnetic state (T = 380 K) in absence of any external magnetic field to remove any magnetic history of the previous measurements of the sample, if present. For the sake of clarity some of the selected magnetic isotherms especially at the low temperature region are given in Fig. 2(B). The magnetic isotherms though exhibit almost linear nature due to the predominant response of antiferromagnetic background matrix, the numerical values indicate that with increasing temperature, magnetization decreases. Such decreasing nature at higher value of temperature correspond the responses of the ferromagnetic droplets presents within the antiferromagnetic matrix. From the linear fitting of the magnetic isotherms (at the high field region, H > 4 T), the extracted spontaneous magnetization (as mentioned earlier) is given in lower inset of Fig. 2(A). Regarding this context, it is worth mentioning that for a canted antiferromagnetic ground state, though the magnetization values decreases with increasing temperature but the nature of field dependent magnetization is different [4].

Another powerful tool to probe the magnetic state of a magnetic material is the study of magnetocaloric effect [30,31]. The magnetocaloric entropy change (-ΔS) was calculated from magnetic isotherms, using Maxwell's thermodynamic relation

$$\Delta S = \int_0^H (\partial M/\partial T) dH$$
$$\Delta S(\frac{T_1+T_2}{2}) = \frac{1}{T_2 - T_1}\int_0^H (M(T_2,H) - M(T_1,H)) dH \quad (1)$$

The temperature dependent magnetocaloric entropy change (-ΔS) at different magnetic fields is shown in Fig. 3. In the magnetic entropy change, the signature of the usual charge ordering (T ~ 270 K) and antiferromagnetic ordering (T ~ 150 K) with lowering the temperature is clearly reflected. Additionally, at the low temperature region (T ~ 50 K), a pronounced peak is found. This peak is not prominent in the magnetization measurements (M(T)). The enlarged views of the magnetocaloric entropy change (at higher and lower field values) are shown in the insets of Fig. 3. Qualitatively the nature of the curve in this region indicates the presence of the ferromagnetic fraction of the compound. Moreover, upon further lowering the temperature (T < 30 K), rapidly increasing nature of magnetic entropy change is found (along positive direction of -ΔS(T) curve). This nature physically implies that along with the core spin of ferromagnetic droplets, uncompensated surface spins of the ferromagnetic droplets and spins of SPM clusters are now getting more oriented along the magnetic field direction when the temperature is reduced further.

Another generic property of the phase separated manganite compounds is the magnetic 'training effect' as reported by Pi et al. [32]. From the magnetic measurements, training effect is ascribed to the reduction of the magnetization due to the magnetic field cycling. Magnetization of the sample was recorded at T = 2 K and 80 K temperature by the field cycling as: H (0) → H (7 T) → H (−7 T) → H (7 T). Enlarged view of the magnetization in the 1^{st} quadrant in first cycle and 2^{nd} cycle are given in Fig. 4.

During the discussion of the training effect in this compound it should be mentioned that since the ferromagnetic droplets (having a very small fraction in quantity) exist within the antiferromagnetic background, difference between the 1^{st} and 2^{nd} cycle is very small. Most important aspect is that at T = 2 K temperature, in the 2^{nd} cycle, magnetization is slightly higher compared to the 1^{st} cycle. Whereas, at T = 80 K, the opposite nature is found (magnetization decreases in 2^{nd} cycle) and the so called training effect is observed. At very low temperature (2 K) since the ferromagnetic interaction is also present, the magnetization increases with the field cycling, whereas at higher temperature (80 K) region, the ferromagnetic interaction is no more and hence training effect is observed. Such nature of the phase separated compound was also reported in earlier study [32].

The overall experimental observations and the discussion about the microscopic view of the low temperature magnetic state of the robust charge ordered $Sm_{0.5}Ca_{0.5}MnO_3$ compound is given in the schematic diagram in Fig. 5. A small fraction of the ferromagnetic droplets appears within the antiferromagnetic matrix along with the superparamagnetic and uncompensated surface spins (associated with the droplets) with random nature. The schematic diagrams below and above of the formation of ferromagnetic droplets are shown in Fig. 5(A) and (B) respectively. Hence, when the temperature decreases (below T ∼ 30 K in the presence of non zero magnetic field), the surface spins get more oriented, resulting in the increasing nature of the magnetocaloric entropy change (positive value of -ΔS) with lowering the temperature. Such droplets formation (dimension ∼2 nm) in same compound was reported earlier from the exchange bias measurements by Dasgupta et al. [33].

4. Conclusions

To summarize, we have made an attempt to describe the nature of the low temperature magnetic state of $Sm_{0.5}Ca_{0.5}MnO_3$ compound *via.* the study of magnetization and magnetocaloric effect. Our experimental results and discussions reveal that at the low temperature regime, a small ferromagnetic fraction and suparamagnetic counterparts are present within the antiferromagnetic matrix. Although determination of the ferromagnetic component was not straight forward from the magnetization measurements, from the magnetocaloric effect study, the nature of this phase at low temperature has been clearly revealed.

Acknowledgements

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References

[1] S.W. Cheong, H.Y. Hwang, Contribution to colossal magnetoresistance oxides, in: Y. Tokura (Ed.), Monographs in Condensed Matter Science, Gordon and Breach, London, 1999.
[2] Y. Tokura (Ed.), Colossal Magnetoresistive Oxides, Gordon and Breach Science, Amsterdam, 2000.
[3] C.N.R. Rao, R. Raveau (Eds.), Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides, World Scientific, Singapore, 1998.
[4] K. Das, T. Paramanik, I. Das, J. Magn. Magn. Matter 374 (2015) 707710.
[5] K. Das, S. Banik, I. Das, Mater. Res. Bull. 73 (2016) 256260.
[6] K. Das, R. Rawat, B. Satpati, I. Das, Appl. Phys. Lett. 103 (2013) 202406.
[7] K. Das, I. Das, J. Appl. Phys. 117 (2015) 175103.
[8] D. Mohan Radheep, P. Sarkar, S. Arumugam, R. Suryanarayanan, P. Mandal, J. Magn. Magn. Mattr. 365 (2014) 51.
[9] K. Das, B. Satpati, I. Das, RSC Adv. 5 (2015) 27338.
[10] A. Banerjee, Kranti Kumar, P. Chaddah, J. Phys. Condens. Matter 21 (2009) 026002.
[11] Y. Tomioka, A. Asamitsu, H. Kuwahara, Y. Moritomo, Y. Tokura, Phys. Rev. B 53 (1996) R1689.
[12] T. Zhang, X.P. Wang, Q.F. Fang, X.G. Li, Appl. Phys. Rev. 1 (2014) 031302.
[13] T. Zhang, E. Zhukova, B. Gorshunov, D. Wu, A.S. Prokhorov, V.I. Torgashev, E.G. Maksimov, M. Dressel, Phys. Rev. B 81 (2010) 125132.
[14] T. Zhang, T.F. Zhou, T. Qian, X.G. Li, Phys. Rev. B 76 (2007) 174415.
[15] G. Jeffrey Snyder, R. Hiskes, S. DiCarolis, M.R. Beasley, T.H. Geballe, Phys. Rev. B 53 (1996) 14434.
[16] Y. Tokura, Y. Tomioka, J. Magn. Magn Mater. 200 (1999) 1.
[17] N.S. Bingham, P. Lampen, M.H. Phan, T.D. Hoang, H.D. Chinh, C.L. Zhang, S.W. Cheong, H. Srikanth, Phys. Rev. B 86 (2012) 064420.
[18] P. Lampen, A. Puri, M.H. Phan, H. Srikanth, J. Alloy. Comp. 512 (2012) 9499.
[19] P. Lampen, N.S. Bingham, M.H. Phan, H. Kim, M. Osofsky, A. Pique, T.L. Phan, S.C. Yu, H. Srikanth, Appl. Phys. Lett. 102 (2013) 062414.
[20] M.H. Phan, S. Chandra, N.S. Bingham, H. Srikanth, C.L. Zhang, S.W. Cheong, T.D. Hoang, H.D. Chinh, Appl. Phys. Lett. 97 (2010) 242506.
[21] M.H. Phan, S.C. Yu, J. Magn. Magn Mater. 308 (2007) 325.
[22] S. Jin, T.H. Tiefel, M. McCormack, R.A. Fastnacht, R. Ramesh, L.H. Chen, Science 264 (1994) 413.
[23] K. Das, P. Dasgupta, A. Poddar, I. Das, Sci. Rep. 6 (2016) 20351.
[24] T. Terai, T. Sasaki, T. Kakeshita, T. Fukuda, T. Saburi, Phys. Rev. B 61 (2000) 3488.
[25] X. Xu, Y. Li, F. Hou, Q. Cheng, R. Su, J. Alloy. Comp. 628 (2015) 89–96.
[26] S.K. Giri, A. Poddar, T.K. Nath, AIP Adv. 1 (2011) 032110.
[27] S.K. Giri, S.M. Yusuf, M.D. Mukadam, T.K. Nath, J. Appl. Phys. 115 (2014) 093906.
[28] S. Banik, K. Das, I. Das, J. Magn. Magn. Mater. 403 (2016) 36–40.
[29] J. Lopez, O.F. de Lima, J. Appl. Phys. 94 (2003) 4395.
[30] A. Biswas, T. Samanta, S. Banerjee, I. Das, Appl. Phys. Lett. 92 (2008) 212502.
[31] P. Lampen, N.S. Bingham, M.H. Phan, H. Srikanth, H.T. Yi, S.W. Cheong, Phys. Rev. B 89 (2014) 144414.
[32] L. Pi, J. Cai, Q. Zhang, S. Tan, Y. Zhang, Phys. Rev. B 71 (2005) 134418.
[33] P. Dasgupta, K. Das, S. Pakhira, C. Mazumdar, S. Mukherjee, S. Mukherjee, A. Poddar, Sc. Rep. 7 (2017) 3220.