Impacts of nanostructuring and magnetic ordering of Nd^{3+} on the magnetic and magnetocaloric response in NdMnO_3

Sayan Chandra⁺, Anis Biswas[#], Manh-Huong Phan and Hariharan Srikanth

Department of Physics, University of South Florida, Tampa, FL 33620, USA

Abstract:

Magnetocaloric properties of NdMnO_3 were investigated in its bulk polycrystalline and nanocrystalline forms. The nanocrystalline sample (average particle size ~ 40 nm) exhibits a maximum in the temperature dependence of magnetic entropy change $[-\Delta S_M(T)]$ at ~ 70 K due to the paramagnetic to ferromagnetic transition, which is absent in case of its bulk counterpart. The absence of peak in $-\Delta S_M(T)$ in the bulk sample is attributed to the co-existence of antiferromagnetic and ferromagnetic phases. A canted magnetic state (CMS) is stabilized at low temperature for both the samples due to the ordering of Nd^{3+} giving rise to a peak in $-\Delta S_M(T)$ at ~ 15 K. Interestingly $-\Delta S_M(T)$ for these two samples show a universal behavior near their transitions at low temperature although their temperature dependence of magnetization is markedly different around those transitions. A detailed analysis of magnetocaloric data conclusively establishes the existence of a canted magnetic state, which is not obvious from magnetometry, demonstrating the usefulness of this method for probing phase coexistence and multiple magnetic states in complex oxide systems.

Keywords: Complex oxides, Magnetism, Magnetocaloric effect

⁺ **Present address:** ÉNERGIE MATÉRIAUX TÉLÉCOMMUNICATIONS, INRS, 1650, boulevard Lionel-Boulet
Varennnes Québec J3X 1S2 Canada

[#] **Present address:** Ames Laboratory, Iowa State University, Ames, IA 50011, USA.

E-Mail addresses: schandr5@mail.usf.edu (S.C), biswas.anis@gmail.com (A.B), phanm@usf.edu (M.H.P),
sharihar@usf.edu (H.S)

1. Introduction:

The study of magnetocaloric properties of materials is an intriguing area of research from the standpoint of both application and basic understanding [1-3]. Owing to its high cooling efficiency, environmental friendliness, and compactness, magnetic refrigeration based on the magnetocaloric effect (MCE) is considered as a promising alternative to conventional gas compression refrigeration techniques [1]. Since the MCE is characterized by the magnetic entropy change (ΔS_M), which is calculated from the derivative of magnetization with respect to temperature ($\partial M/\partial T$) via the Maxwell equation, a systematic study of the magnetic field and temperature dependences of ΔS_M has been proved to be more useful in probing the nature of magnetic phase transition and ground state properties of magnetic systems, as compared to conventional magnetometry studies [4-6].

Rare-earth based manganites with a general formula of $R_{1-x}B_xMnO_3$ (where R is rare-earth, B is bivalent ion) belonging to the class of strongly correlated electron systems exhibit rich complexity in their physical properties [7]. In addition to the discovery of so-called colossal magnetoresistance (CMR), the recent findings of giant magnetocaloric effect (MCE) in these materials make them very promising candidates for magnetic refrigeration applications [3]. There is a recent trend of research in this direction to understand the effect of reduction of particle size on the magnetic and magnetocaloric properties of manganites [4, 8-13]. It has been shown that the magnetic and magnetocaloric properties of these systems are markedly modified when the materials are synthesized in the nanostructured form. The magnetic transition temperature along with ΔS_M can be tuned by varying particle size, and the refrigerant capacity (RC) – an important magnetocaloric figure of merit - enhances in some systems as a result of the reduction in particle size to the nanoscale [9,10]. In addition, recent studies have revealed that MCE can be exploited in precise determination of a magnetic transition in case of nanoparticles even if the transition is too weak to be detected by conventional temperature-dependent magnetization or resistivity measurements [4].

Among the entire family of manganites, compounds without any bi-valent doping are prototypical parent compounds, which form the basis of intense research in this subject. These

systems are antiferromagnetic in their ground states, due to a strong Jahn-Teller effect and also Mott insulators [7, 14]. A typical example of undoped manganites is NdMnO_3 . Ideally it exhibits a paramagnetic (PM) to antiferromagnetic (AFM) transition around 70 K during cooling, thus resulting in stabilization of an antiferromagnetic ground state. Besides this, Nd^{3+} ions in this compound order at low temperature, thus modifying the AFM state to a canted magnetic state (CMS), which has ferromagnetic-like features [15-19]. The stabilization of the AFM state at 78 K followed by a formation of CMS at 13 K was probed by neutron diffraction study by Munoz et al. [15]. Other neutron diffraction studies also confirm the AFM transition as well as the ordering of Nd^{3+} in this compound [16-18].

The main objective of our present work is to investigate the impacts of nanostructuring and Nd^{3+} ordering on the magnetic and magnetocaloric properties of undoped NdMnO_3 . In this regard, a comprehensive study has been performed on NdMnO_3 in both the polycrystalline bulk and nanocrystalline forms. We have observed that the nanocrystalline NdMnO_3 exhibits an appreciably large MCE in two temperature regions (two peaks in $-\Delta S_M$ vs. T curves), whereas its bulk counterpart shows a single maximum in $-\Delta S_M(T)$ indicating a considerable modification of the magnetic and magnetocaloric properties of this material due to the reduction in average particle size. The ordering of Nd^{3+} has been found to impact the magnetic structure of NdMnO_3 at low temperature, but the effect is completely different in the nanocrystalline sample in comparison with its bulk polycrystalline counterpart.

2. Sample preparation and characterization:

Nanocrystalline NdMnO_3 samples were synthesized by sol-gel method from the stoichiometric ratio of Nd_2O_3 and MnO_2 using the procedure described in an earlier study [20]. At the end of the sol-gel process, the decomposed gel was heat treated at 1000 °C in air for 6 hrs. The formation of the crystalline form of the samples was confirmed by X-ray diffraction (XRD) study. Figure 1 shows a typical XRD pattern of the nanocrystalline sample. Transmission electron microscopy (TEM) was employed to determine the average particle size (d_{av}) of the nanocrystalline sample. The average particle size determined from the TEM images to be ~ 36 nm (± 8 nm), which matches well with that calculated from the XRD patterns using Scherrer formula [21]. A typical TEM image of the nanocrystalline sample is shown in the inset of Fig. 1. For a proper comparison, a polycrystalline (bulk) sample was prepared from one part of the same decomposed

gel used for the nanocrystalline sample by annealing it at 1400 °C for 36 hrs. The formation of bulk sample was also confirmed by x-ray diffraction study [inset (a), Fig.1].

3. Experimental results and discussions:

A commercial Physical Property Measurement System (Quantum Design) equipped with a vibrating sample magnetometer (VSM) was utilized to investigate the magnetic properties of the prepared samples. Fig. 2 shows the temperature dependence of magnetization for both bulk and nanocrystalline samples measured in a field-cooled protocol in the presence of a 5 mT magnetic field. It can be seen that there is no clear signature of a magnetic transition to an AFM state in $M(T)$ curves for the samples. However, a broad anomaly in $M(T)$ is visible at ~ 70 K for the bulk sample. This can arise from the fact that the undoped manganites often possess a small amount of cationic vacancies depending on their preparation condition, which eventually creates Mn^{4+} ions thus inducing ferromagnetism via double exchange (DE) interactions between Mn^{3+} and Mn^{4+} ions [22-25]. The presence of these cationic vacancies is commonly known as “self-doping” effect and reflected in a slight variation in the oxygen content from an ideal value of “3”. The AFM interaction in these systems can thus be considerably weak, resulting in the hindrance of an AFM transition due to self-doping. Since self-doping is a very common consequence in undoped manganites, it is reasonable to state that this effect is mainly responsible for weakening AFM in our present samples. In addition to this, surface effect becomes significant as particle size is reduced to the nanoscale and this can also strengthen DE interactions in the nanocrystalline AFM samples as pointed out in previous studies [26,27]. It is also noted that the magnetization of the nanocrystalline sample starts to increase below ~ 70 K, a typical feature of a PM to FM transition.

At low temperature below ~ 15 K, both the samples undergo a magnetic transition. For the bulk sample, the transition leads to an increase of magnetization (M), which apparently indicates the stabilization of a FM-like state. In contrast to that, M drops at low temperature for the nanocrystalline sample, suggesting a suppression of the pre-existing ferromagnetism in this system. Since the ordering temperature of Nd^{3+} is ~ 15 K for $NdMnO_3$ as mentioned earlier, [ref. 15-19] one can argue that the transitions at low temperatures for the samples are related to Nd^{3+} ordering. This intriguing feature will be discussed later. We also measure $M(T)$ curves at

different magnetic fields (inset(a), Fig. 2). All the curves clearly indicate existences of two transitions for the nanocrystalline sample : one at ~ 60 K (M starts to increase) and other at ~ 15 K (M starts to be suppressed).

To assess the nature of phase transitions and magnetocaloric effects in these samples, the isothermal magnetic field dependence of magnetization $[M(H)]$ was measured in different temperatures . $M(H)$ curves at selected temperatures are shown in Fig. 3(a,b), and their corresponding Arrott plots i.e., H/M vs. M^2 , are shown in insets of Fig.3(a,b). The H/M vs M^2 curves show positive slopes, indicating the second-order nature of the phase transitions, according to Banerjee's criterion [28]. The magnetocaloric parameter ΔS_M has been calculated from a family of isothermal $M(H)$ curves using the following Maxwell relation [1]:

$$\left[\frac{\partial S(T,H)}{\partial \mu_0 H} \right]_T = \left[\frac{\partial M(T,H)}{\partial T} \right]_{\mu_0 H} \quad (1)$$

The temperature dependence of $-\Delta S_M$ for different magnetic fields for the bulk and nanocrystalline samples are shown in Fig.4a and Fig. 4b respectively. For bulk NdMnO_3 , a positive peak of $-\Delta S_M(T)$ is observed at ~ 15 K, with an appreciably large value of maximum entropy change ($\Delta S_{\text{max}} \sim 4.4$ J/kg K) . On the other hand, two distinct maxima appear in $-\Delta S_M(T)$ for the nanocrystalline sample at ~ 70 K and 15 K, indicating a significant modification of the magnetocaloric response of the system due to the reduction of particle size. The values of ΔS_{max} at ~ 70 K and 15 K are ~ 2.6 J/kg K and 4.4 J/kg K. Interestingly, the value of ΔS_{max} at low temperature is similar for these samples. It has been established that the value of $-\Delta S_M$ is positive for materials exhibiting a PM-FM transition because of the fully magnetically ordered configuration with the application of an external magnetic field. Negative values of $-\Delta S_M$ are found in AFM ordered systems due to an orientation disorder of the magnetic sublattice anti-parallel to the applied magnetic field [1]. Thus the observed positive maxima in $-\Delta S_M(T)$ suggest the magnetic transitions that lead to the stabilization of FM-like states in the present samples.

We recall that a ferromagnetic-like CMS can develop and possess most of the macroscopic features of a conventional FM state in undoped manganites [15-18]. The CMS state can arise from (i) an interplay between competing DE and super exchange interactions and/or (ii) ordering of rare-earth ions [19, 29-30]. The transition to a CMS state is difficult to be distinguished from

the FM transition. Thus the transitions in the present samples, which look apparently ferromagnetic from the nature of $-\Delta S_M(T)$, may also be ascribed to stabilization of CMS.

As the ground states of undoped manganites are often of AFM, the possibility of some AFM correlation that exists even in case of slightly oxygen rich compounds may not be ruled out. If the AFM interaction is weak enough to dominate over ferromagnetism, one can expect a positive maximum in $-\Delta S_M(T)$ also. We have calculated $-\Delta S_M(T)$ for very low magnetic fields. Interestingly, a small negative $-\Delta S_M(T)$ is obtained in case of the bulk sample for magnetic fields less than 20 mT in the temperature range ~ 50 -60 K. The negative $-\Delta S_M$ in presence of magnetic field is called inverse magnetocaloric effect (IMCE), which can arise either due to a structural transition or due to presence of an AFM correlations [1,10,31-33]. We have checked that H/M vs. M^2 even in the low magnetic field region has no negative slope, ruling out any magnetic field induced first-order transition. Thus the positive ΔS_M in this case indicates that a fraction of the AFM phase exists in the bulk sample along with the FM state. As the relative contribution of AFM to $-\Delta S_M(T)$ is opposite to that of FM, any distinct maximum is not observed in its $-\Delta S_M(T)$ in the temperature range around 70 K when a higher magnetic field is applied. Only at very low magnetic fields (below 20 mT), the contribution due to the AFM fraction slightly dominates over FM, resulting in the observed IMCE. From these analyses and foregoing discussions, it can be concluded that the magnetic state of the bulk sample comprises both AFM and FM phases below ~ 70 K. The transition from the PM state to a FM-like state is also evidenced through a broad anomaly in $M(T)$ in that temperature region (Fig. 2).

In complete contrast to the bulk sample, the nanocrystalline sample does not show any positive $\Delta S_M(T)$ even in the presence of low magnetic fields, implying that its transition at ~ 70 K is a more conventional transition from the PM to FM state, in the absence of an AFM phase. This PM-FM transition leads to a clear, positive peak in $-\Delta S_M(T)$ at ~ 70 K, which is absent in case of the bulk sample.

Recently Franco et al. have demonstrated that the magnetic entropy change of a system associated with a second order magnetic phase transition follows a universal behaviour [34-36]. The normalized $\Delta S_M(T)$ (normalized to $\Delta S_{\max}$) vs. reduced temperature, θ (defined as eqn 2) curves measured for different applied magnetic fields collapse onto a single universal curve,

which is unique for each universality class, regardless of a particular specimen [34-36]. θ is defined as [35],

$$\theta = (T - T_p)/(T_r - T_p) \quad (2)$$

where T_p is the temperature corresponding to $\Delta S_{\max}$, T_r is the reference temperature corresponding to a certain fraction f that fulfils $\Delta S_M(T_r)/\Delta S_{\max} = f$. Although the universal behavior was initially proposed on a phenomenological basis, it has recently been grounded by theory [36]. There have been many reports indicating the construction of universal curves for different types of magnetic materials [36-39]. Interestingly, the same universal curve can describe magnetic entropy change at low temperature for the present samples in spite of the nature of their $M(T)$ corresponding to the transition at ~ 15 K being entirely different. From the observed universal behavior, it can be inferred that such a transition at low temperature renders the systems to have a similar magnetic state.

A question emerges concerning the origin of the transition at ~ 15 K. We have carried out a temperature-dependent XRD study on the present samples (not shown here), and do not observe any signature of a structural transition around 15 K, thus ruling out the perspective that the observed low temperature transition at $M(T)$ and $\Delta S_M(T)$ are attributed to the structural phase transitions. As we already noted above, the ordering temperature of Nd^{3+} in case of bulk NdMnO_3 is ~ 15 K [15-19]. Such an ordering can cause the formation of a FM-like CMS for the present samples. In our case the ordering of Nd^{3+} is the most plausible reason for the occurrence of the transition at 15 K. However the magnetic state before this transition is different for the two samples. For the bulk sample, a magnetic state comprising FM and AFM phases is developed below 70 K, which is transformed to the FM-like CMS at a low temperature below 20 K. As a result, M starts to increase below this temperature. Conversely, Nd^{3+} leads to the transition from the pre-existing FM state to CMS state in the nanocrystalline system, giving rise to the suppression of the magnetization (Fig. 2). As CMS is FM-like we have observed the positive maxima in $-\Delta S_M(T)$ for both cases and the magnetic entropy change also follows the same universal curve.

To get further insight into the magnetic properties of these materials, we calculated $-\Delta S_M(T)$ theoretically on the basis of Landau theory of phase transitions [40-42]. According to Landau theory, the Gibbs free energy can be expressed as,

$$G(T, M) = G_0 + \frac{1}{2}AM^2 + \frac{1}{4}BM^4 - MH \quad (3)$$

where A and B are functions of T. Subsequently, the magnetic equation of state and ΔS_M around transition can be expressed by the following equations:

$$\frac{H}{M} = A + BM^2 \quad (4)$$

$$\Delta S_M = -\frac{1}{2} \frac{\partial A}{\partial T} M^2 - \frac{1}{4} \frac{\partial B}{\partial T} M^4 \quad (5)$$

It has been argued that positive value of B is an indication of the second order transition [40]. The parameters A(T) and B(T) were obtained from the linear regions of H/M versus M^2 plots following equation (4), which are shown in insets of Fig. 6. For both the samples, B is positive in entire range of temperature. Hence the magnetic transitions associated with these samples are of second order in nature. For the bulk sample A decreases with the decrease of temperature. There is a slight change of slope at A(T) curve near the low temperature transition. B(T) for the sample has a broad hump at the temperature range near 70 K and there is a tendency of upturn of B at the low temperature. On the other hand, for the nanocrystalline sample, both A(T) and B(T) have slight changes of slope near its two transitions.

Using the obtained A(T) and B(T), the temperature dependence of ΔS_M can be calculated from equation (5), which has been shown in Fig. 6 for a 5 T magnetic field change. It has been reported that ferromagnetic manganites with a second order phase transition, $\Delta S_M(T)$ calculated from Landau theory according to equation (5) agrees quite well with experimental results [40-41]. For the present bulk NdMnO_3 , the theoretically calculated $-\Delta S_M(T)$ in the vicinity of the transition at ~15 K deviates considerably from the experimentally obtained $-\Delta S_M(T)$. This further proves that the transition is not a conventional PM-FM transition as discussed above. The

experimentally obtained value of $-\Delta S_{\max}$ is smaller than the theoretically calculated one, suggesting that the transition leads to CMS, not fully FM state. However for the nanocrystalline sample, the theoretically calculated $-\Delta S_M(T)$ matches quite well with the experimental curve around the transition at ~ 70 K, consistent with the perspective that the PM to FM transition appeared to occur at this temperature. Since the FM state was converted to CMS due to Nd^{3+} ordering at ~ 15 K, a discrepancy between the theoretical and experimental $-\Delta S_M(T)$ results at low temperature for this sample is understandable.

4. Conclusions

We have carried out a detailed, comparative study of the magnetic and magnetocaloric properties of polycrystalline (bulk) and nanocrystalline NdMnO_3 samples. For the bulk sample, only one maximum was observed in $-\Delta S_M(T)$ at low temperature with an appreciable value of $-\Delta S_{\max}$. However, two peaks appeared in $-\Delta S_M(T)$ for the nanocrystalline sample. The stabilization of CMS at low temperature due to Nd^{3+} ordering is assessed through a detailed analysis of the magnetocaloric data. A universal master curve can be constructed to describe the magnetic entropy change at low temperature for both the samples. The presence of AFM and FM phases in the bulk sample is evident from the MCE analysis, which cannot be realized by conventional magnetization vs. temperature measurements. Our study demonstrates the usefulness of the magnetocaloric method to acquire fundamental insights into the complex magnetic structures of magnetic materials in addition to its technological relevance.

Acknowledgements:

The work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award # DE-FG02-07ER46438.

References

1. A.M. Tishin, in *Handbook of Magnetic Materials*, vol. 12, ed. by K.H.J. Buschow Elsevier, Amsterdam, 1999, p. 395.
2. K. A. Gschneidner Jr., V. K. Pecharsky, A. O. Tsokol,
Recent developments in magnetocaloric materials,
Rep. Prog. Phys. 68 (6) (2005) 1479
3. M. H. Phan, S. C. Yu,
Review of the magnetocaloric effect in manganite materials,
J. Magn. Magn. Mat. 308 (2) (2007) 325-340
4. A. Biswas, T. Samanta, S. Banerjee, I. Das,
Influence of charge ordering on magnetocaloric properties of
nanocrystalline $\text{Pr}_{0.65}(\text{Ca}_{0.7}\text{Sr}_{0.3})_{0.35}\text{MnO}_3$, Appl. Phys. Lett. 92 (21) (2008) 212502
5. T. Samanta, I. Das, S. Banerjee,
Comparative studies of magnetocaloric effect and magnetotransport behavior
in GdRu_2Si_2 compound, J. Appl. Phys. 104 (12) (2008) 123901
6. M. H. Phan, M. B. Morales, N. S. Bingham, H. Srikanth, C. L. Zhang, S. -W. Cheong,
Phase coexistence and magnetocaloric effect in $\text{La}_{5/8-y}\text{Pr}_y\text{Ca}_{3/8}\text{MnO}_3$ ($y=0.275$),
Phys. Rev. B 81 (2010) 094413
7. Y. Tokura (Ed.) 2000 *Colossal Magnetoresistive Oxides* (Gordon and Breach Science Publishers, The Netherlands).
8. W. J. Lu, X. Luo, C. Y. Hao, W. H. Song, Y. P. Sun,
Magnetocaloric effect and Griffiths-like phase in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ nanoparticles
J. Appl. Phys. 104 (11) (2008) 113908
9. A. Biswas, T. Samanta, S. Banerjee, I. Das,
Magnetocaloric properties of nanocrystalline $\text{Pr}_{0.65}(\text{Ca}_{0.6}\text{Sr}_{0.4})_{0.35}\text{MnO}_3$,

- J. Appl. Phys. 103 (1) (2008) 013912
10. M. H. Phan, S. Chandra, N. S. Bingham, H. Srikanth, C. L. Zhang, S. W. Cheong, T. D. Hoang, H. D. Chinh,

Collapse of charge ordering and enhancement of magnetocaloric effect in nanocrystalline $\text{La}_{0.35}\text{Pr}_{0.275}\text{Ca}_{0.375}\text{MnO}_3$,
Appl. Phys. Lett. 97 (24) (2010) 242506
 11. A. Biswas, T. Samanta, S. Banerjee, I. Das,

Magnetocaloric properties of nanocrystalline $\text{La}_{0.125}\text{Ca}_{0.875}\text{MnO}_3$,
Appl. Phys. Lett. 94 (23)(2009) 233109
 12. P. Lampen, A. Puri, M. H. Phan, H. Srikanth ,

Magnetocaloric properties of nanocrystalline $\text{La}_{0.125}\text{Ca}_{0.875}\text{MnO}_3$,
J. Alloy. Comp. 512 (1) (2012) 94
 13. A. Rostamnejadi, M. Venkatesan, J. Alaria, M. Boese, P. Kameli, H. Salamati, J. M. D. Coey,

Conventional and inverse magnetocaloric effects in $\text{La}_{0.45}\text{Sr}_{0.55}\text{MnO}_3$ nanoparticles,
J. Appl. Phys. 110 (4) (2011) 043905
 14. J.M.D. Coey, M. Viret, S. von Moller,

Mixed Valence Manganites, Adv. in Phys. 48 (2) (1999) 167
 15. A. Munoz, J. A. Alonso, M. J. Martinez-Lope, J. L. Garcia-Munoz, M. T. Fernandez-Diaz,

Magnetic structure evolution of NdMnO_3 derived from neutron diffraction data, J. Phys.: Cond. Mat. 12 (7) (2000) 1361
 16. T. Chatterji, B. Ouladdiaf, D. Bhattacharya,

Neutron diffraction investigation of the magnetic structure and magnetoelastic effects in NdMnO_3 ,
J. Phys. : Cond. Mat. 21 (30) (2009) 306001
 17. S. Y. Wu, C. M. Kuo, H. Y. Wang, W.-H. Li, K. C. Lee, J. W. Lynn, R. S. Liu,

Magnetic structure and spin reorientation of the Mn ions in NdMnO_3 ,
J. Appl. Phys. 87 (9) (2000) 5822

18. T. Chatterji, B G.J. Schneider, L. Van Eijck, B. Frick, D. Bhattacharya
Direct evidence for the Nd ordering in NdMnO₃ from hyperfine splitting of Nd nuclear levels, J. Phys. : Cond. Mat. 21 (12) (2009) 126003
19. A. Biswas, I. Das,
Magnetic and transport properties of nanocrystalline Nd_{0.5}Sr_{0.5}MnO₃, J. Appl. Phys. **102** (6) (2007) 064303
20. A. Biswas, I.Das, C. Majumdar ,
Modification of the charge ordering in Pr_{1/2}Sr_{1/2}MnO₃ nanoparticles, J. Appl. Phys. 98 (12) (2005) 124310
21. B. E. Warren 1969 *X-ray Diffraction* (Addison-Wesley, New York)
22. S. Chandra, A. I. Figueroa, Barnali Ghosh, M. H. Phan, H. Srikanth, and A. K. Raychaudhuri
Phase coexistence and magnetic anisotropy in polycrystalline and nanocrystalline LaMnO_{3+δ}
J. Appl. Phys. 109 (7) (2011) 07D720
23. P A Joy, C Raj Sankar , S K Date
The origin of ferromagnetism in LaMnO_{3+δ},
J. Phys.: Cond. Mat. 14 (19) (2002) 4985
24. R. Iaiho, K.G. Iisunov, E. Lahderanta, P.A. Petrenko, J. Salminen, V.N. Stamov, Yu.P. Stepanov, V.S. Zakhvalinski
Low-field magnetic properties of LaMnO_{3+δ} with 0.065 ≤ δ ≤ 0.154
J. Phys. and Chem. of Solids 64 (12) (2003) 2313
25. S. Chandra, A. Biswas, S. Datta, B. Ghosh, V. Siruguri, A. K. Raychaudhuri, M. H. Phan, H. Srikanth
Evidence of a canted magnetic state in self-doped LaMnO_{3+δ} (δ = 0.04): a magnetocaloric study
J. Phys. : Cond. Mat. 24 (36) (2012) 366004
26. S. Dong, R. Yu, S. Yunoki, J. M. Liu, E. Dagotto

Ferromagnetic tendency at the surface of CE-type charge-ordered manganites
Phys. Rev.B 78 (2008) 064414

27. V. Dwivedi, A. Taraphder,

Unusual ferromagnetism in nanoparticles of doped oxides and manganites,
Sol. Stat. Comn. 151 (24) (2011) 1999

28. B. K. Banerjee

On a generalised approach to first and second order magnetic transitions
Phys. Lett. 12 (1) (1964) 16

29. C. Ritter, M. R. Ibarra, J. M. De Teresa, P. A. Algarabel, C. Marquina, J. Blasco, J. Garcia,
S. Oseroff, S-W. Cheong

Influence of oxygen content on the structural, magnetotransport, and magnetic properties
of $\text{LaMnO}_{3+\delta}$
Phys. Rev. B 56 (1997) 8902

30. O. Crisan, M. Angelakeris, N. K. Flevaris, G. Filoti

Magnetism and anisotropy in core-shell nanoparticles
J. Optoelectron. Adv. Mater. 5 (4) (2003) 959

31. P J von Ranke, N A de Oliveira, B P Alho, E J R Plaza, V S R de Sousa, L Caron, M S Reis

Understanding the inverse magnetocaloric effect in antiferro- and ferrimagnetic arrangements
J. Phys.: Cond. Mat. 21(5) (2009) 056004

32. T. Krenke, E. Duman, M. Acet, E. F. Wassermann, X. Moya, L. Manosa, A. Planes

Inverse magnetocaloric effect in ferromagnetic Ni–Mn–Sn alloys
Nat. Mat. 4 (6) (2005) 450-454

33. A. Biswas, S. Chandra, T. Samanta, B. Ghosh, S. Datta, M. H. Phan, A. K. Raychaudhuri, I.
Das, H. Srikanth

Universality in the entropy change for the inverse magnetocaloric effect
Phys. Rev. B 87 (2013) 134420

34. V. Franco, J. S. Blazquez, A. Conde

Field dependence of the magnetocaloric effect in materials with a second order phase transition:
A master curve for the magnetic entropy change

- Appl. Phys. Lett. 89 (22) (2006) 222512
35. V. Franco, A. Conde, V. K. Pecharsky, K. A. Gschneidner Jr.
Field dependence of the magnetocaloric effect in Gd and $(\text{Er}_{1-x}\text{Dy}_x)\text{Al}_2$: Does a universal curve exist?
Euro. Phys. Lett. 79 (4) (2007) 47009
36. V. Franco, A. Conde, J. M. Romero-Enrique, J. S. Blázquez
A universal curve for the magnetocaloric effect: an analysis based on scaling relations
J. Phys.: Cond. Mat. 20 (28) (2008) 285207
37. M. H. Phan, V. Franco, A. Chaturvedi, S. Stefanoski, G. Nolas, H. Srikanth
Origin of the magnetic anomaly and tunneling effect of europium on the ferromagnetic ordering in $\text{Eu}_{8-x}\text{Sr}_x\text{Ga}_{16}\text{Ge}_{30}$ ($x=0,4$) type-I clathrates
Phys. Rev. B 84 (2011) 054436
38. V. Franco, R. Caballero-Flores, A. Conde, Q. Y. Dong, H. W. Zhang,
The influence of a minority magnetic phase on the field dependence of the magnetocaloric effect,
J. Magn. Magn. Mat. 321 (9) (2009) 1115
39. C. Marcela Bonilla, J. Herrero-Albillos, F. Bartolome, L. M. Garcia, M. Parra-Borderias, V. Franco
Universal behavior for magnetic entropy change in magnetocaloric materials: An analysis on the nature of phase transitions
Phys. Rev. B **81** (2010) 224424
40. V. S. Amaral, J. S. Amaral
Magnetoelastic coupling influence on the magnetocaloric effect in ferromagnetic materials
J. Magn. Magn. Mat. 272-276 (3) (2004) 2104-2105
41. M. Oumezzine, S. Zemni, O. Pena
Room temperature magnetic and magnetocaloric properties of $\text{La}_{0.67}\text{Ba}_{0.33}\text{Mn}_{0.98}\text{Ti}_{0.02}\text{O}_3$ perovskite

J. Alloys. Comp. 508 (2) (2010) 292-296

Figure captions:

FIG. 1: X-ray diffraction pattern for the nanocrystalline sample. Inset (a): XRD pattern for bulk sample. Inset (b): a typical TEM image of this sample.

FIG 2: Temperature dependence of magnetization for the bulk and nanocrystalline samples. Magnetization measurement was carried out in a field cooled protocol in the presence of a 0.005T field. For the nanocrystalline sample, the magnetization starts to decrease at ~ 15 K as indicated by an arrow. Inset(a): $M(T)$ curves for nanocrystalline sample measured in different fields in field cooled protocol. Inset (b): a broad anomaly observed in $M(T)$ for the bulk sample at ~ 70 K as indicated by an arrow.

FIG. 3: M vs. H curves for selected temperatures for (a) bulk and (b) nanocrystalline samples. Insets: The Arrot plots for these samples.

FIG.4: Temperature dependence of the magnetic entropy change for different magnetic field changes for (a) bulk (b) nanocrystalline samples. Inset in Fig. 4(a): $-\Delta S_M$ vs. T obtained for the bulk sample for low magnetic field changes (up to a 20 mT).

FIG. 5 : Universal behaviour of normalized $\Delta S_M(T)$ vs. θ (for all magnetic fields) for both the samples in the vicinity of the maximum at ~ 15 K (indicated by an arrow). Inset: an expanded view of the curves near the peak at 15 K.

FIG. 6 : Temperature dependence of $-\Delta S_M$ for a 5 T magnetic field change obtained from the experimentally and theoretically calculated results for (a) bulk and (b) nanocrystalline samples. Insets: Temperature dependence of the parameters A and B (as discussed in the text) used for calculation of the magnetic entropy change from Landau theory.

Figure 1
[Click here to download high resolution image](#)

Fig. 1

Figure 2
[Click here to download high resolution image](#)

Fig. 2

Figure 3
[Click here to download high resolution image](#)

Fig. 3

Figure 4
[Click here to download high resolution image](#)

Fig. 4

Figure 5
[Click here to download high resolution image](#)

Fig. 5

Figure 6
[Click here to download high resolution image](#)