This item was submitted to [Loughborough's Research Repository](#) by the author.
Items in Figshare are protected by copyright, with all rights reserved, unless otherwise indicated.

Origin of hysteresis in La Ca MnO

PLEASE CITE THE PUBLISHED VERSION

<http://dx.doi.org/10.1557/opl.2011.590>

LICENCE

CC BY-NC-ND 4.0

REPOSITORY RECORD

Morrison, Kelly, A. Berenov, and L.F. Cohen. 2019. "Origin of Hysteresis in La Ca Mno". figshare.
<https://hdl.handle.net/2134/12673>.

This item was submitted to Loughborough's Institutional Repository (<https://dspace.lboro.ac.uk/>) by the author and is made available under the following Creative Commons Licence conditions.

For the full text of this licence, please go to:
<http://creativecommons.org/licenses/by-nc-nd/2.5/>

Origin of Hysteresis in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$

K. Morrison¹, A. Berenov², and LF Cohen¹

¹ Blackett Laboratory, Prince Consort Rd, London SW7 2BZ, UK

² Department of Materials Science, Prince Consort Rd, London SW7 2BZ, UK

ABSTRACT

Hysteresis is unattractive for magnetocaloric applications because it introduces loss in the cooling cycle. It is however usually associated with a first order transition and large entropy change. In this paper we review the sources of hysteresis in magnetocaloric materials and in particular in manganite systems where the nature of the transition in terms of whether it is indeed a first order transition remains elusive.

INTRODUCTION

The field of room temperature magnetic refrigeration is beginning to show signs of maturing. A number of promising refrigeration prototypes with large temperature span have been reported within the last twelve months. The most popular systems appear to use one of a small number of compounds including: Gd or Gd based alloys, $\text{Pr}_2\text{Fe}_{17}$, various manganite compositions, $\text{La}(\text{Fe}_y\text{Co}_x\text{Si}_{1-x-y})_{13}$, $\text{Mn}_{1-\delta}\text{As}_{1-x}\text{Sb}_x$ or $\text{MnFeP}_{0.8}\text{Ge}_{0.2}$, for example see [1]. Each material system has attractive aspects but there are some outstanding issues before a robust commercially viable product is developed. One major question is whether magnetic systems showing a first order or second order magnetocaloric transition should be used in these applications. Gd, the ideal prototype material has a second order transition. It has the disadvantage that it is a rare earth and therefore costly, its entropy change is modest although perfectly useable, but the resulting temperature span for a refrigeration cycle is more limited than systems where doping can be used to shift the transition temperature. $\text{La}(\text{Fe}_{1-x}\text{Si}_x)_{13}$ is certainly a tunable system with a T_c typically close to 200K that can be brought to room temperature with Co substitution for Fe[2]-[4], or hydrogenation[5]. It is low cost as it is mainly made of Fe, but there are questions of stability of the hydrogenation process and sample degradation on repeated cycling because of large volume changes associated with the transition itself. It is nevertheless a very promising system. Many of the first order systems suffer from the sample degradation on repeated thermal cycling and in addition many systems also show significant thermal and magnetic hysteresis. $\text{La}(\text{Fe}_{1-x-y}\text{Co}_y\text{Si}_x)_{13}\text{H}$ is rather unique because it clearly shows a first order, field driven metamagnetic transition and yet the intrinsic hysteresis is small. Nevertheless extrinsic sources of hysteresis in this system can be significant, due in part to the large latent heat, large heat capacity and poor thermal conductivity at the metamagnetic transition, as discussed elsewhere [6].

The situation with the manganites $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ (where R is a rare earth) is interesting and their magnetocaloric properties have been investigated [7] and discussed widely [8]. The fundamental understanding associated with these materials was heavily researched in the 1990s and of course being ceramic oxides and components for fuel cell materials, work has been ongoing for many years to establish reliable processing routes to homogeneously doped, and

stable compounds [9-10]. One area that remains outstanding is whether the magnetocaloric transition in these materials is first or second order. There is evidence from electron holography indicating nucleation and growth associated with the development of the ferromagnetic phase which is suggestive of first order behaviour, although the technique only allows the study of a highly thinned edge region of the sample [11]. A second and perhaps related issue is why the observed entropy change is much smaller in some cases, than would be expected simply from the theoretical estimate of the magnetic contribution to the entropy change [12].

Over a number of years we have developed a unique set of characterization probes [13-15] and using these we investigate the source of hysteresis in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ and speculate on the order of the transition.

SOURCES OF HYSTERESIS

Figure 1. Shows the free energy landscape for a first order metamagnetic transition, where U (U') is the magnitude of the energy barrier and M_1 , M_2 are the separate magnetic states. As a guide, the energy barrier can be associated with the magnitude of the magnetic hysteresis ΔH and the change of magnetic state can be associated with the magnitude of the latent heat of the system, as indicated. Figure follows from Kuz'min and Richter [16].

First it is useful to review the sources of hysteresis in a magnetocaloric system. As shown schematically in figure 1, the free energy distribution in a first order system has two energy minima separated by an energy barrier U (or U') [16]. In the field driven magnetocaloric transition, to move the system from one energy minima to the other requires finite field to raise the energy of one of the phases until that the barrier is overcome. Systems where the intrinsic energy barrier U to move from one state to another is high, will naturally have larger magnetic hysteresis ΔH . In the example shown in figure 1 there is a decrease in ΔM and a reduction in the effective energy barrier $U' \rightarrow U$ indicated by the arrows, which can happen in real first order systems due to for example, increasing the temperature of the system. As a guide, the schematic shows that the change in magnetic state can be associated with the magnitude of the latent heat.

Once this basic scenario is established, a number of extrinsic sources of hysteresis can be imagined, particularly when one realizes that the magnetic transition in a disorder broadened first order transition takes place by nucleation or seeding of the new phase in finite nucleation size clusters. The process of transformation from one phase to the other then involves nucleation and growth [14]. Extrinsic contributions to hysteresis related to the impediment to transform from one magnetic phase to another include effects related to the level of disorder within the sample which influences the number of nucleation sites. The energy to grow one phase embedded within another is influenced by magnetostatic and magnetocrystalline energies, but also by large volume changes and local strain fields [17]. As a rule we observe nucleation and growth in systems with large magnetocrystalline anisotropy and large intrinsic magnetic and thermal hysteresis usually associated with strong coupling between a magnetic and structural (or volume) change.

In addition a number of groups have reported dynamic hysteresis effects due to the magnetocaloric effect itself and loss of isothermal conditions. In this case the hysteresis has been shown to have a clear magnetic field sweep rate dependence that is controlled by the sample size [6]. As well as this, the well known superheating and supercooling scenario, where depending on the cooling (heating) rate the system can remain in the higher energy state and overshoot the transition, only dropping to a lower energy state at a lower (higher) temperature or field, can also create an artificial hysteresis with a magnitude dependent on cooling (or heating) rate [17]. Dynamic hysteresis could also be anticipated if strain fields are built up within the sample, although a clear demonstration of this effect has not been established.

EXPERIMENT

Here we study $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (LCM) using powder prepared by solid state synthesis. Stoichiometric amounts of La_2O_3 (Sigma Aldrich, 99.99% metal basis), MnO_2 (Alfa Aesar, 99.9% metal basis), and CaCO_3 (Alfa Aesar, 99.95% metal basis) were used. Prior to weighing La_2O_3 was calcined overnight at 1000 °C and quenched in a desiccator, MnO_2 and CaCO_3 were dried at 300 °C for several hours. Starting powders were mixed, ball milled overnight with zirconia balls in isopropanol and calcined in air at 1150 °C for 4 hrs. The calcinations was repeated after the intermediate grinding. The resulting powder was rotary milled with zirconia balls in isopropanol at 300 RPM for 3 hrs.

The LCM pellet was prepared by uniaxial pressing at 0.75 ton/cm² and sintering in air at 1400 °C for 2 hrs followed by annealing in air at 900°C for 30 hrs in order to equilibrate oxygen content. The pellet was 80% dense with 17% of open porosity as measured geometrically and by the Archimedes method (Sartorius, CP124S).

Crystal structure and phase purity were studied by an X'Pert Pro MPD X-ray diffractometer (PANalytical) using Cu-K α radiation. The "Unitcell" non-linear least-square refinement program [18] was used to calculate the lattice parameters. The particle size distribution curve was measured by Low Angle Laser Light Scattering technique (Coulter, LS230). Sintering behaviour of the powder was studied in air by dilatometer (Netzsch, DIL 402C) with a heating rate 5 °C/min.

Calorimetric Methods

Heat capacity and latent heat measurements have been carried out using a Xensor Integration SiNi membrane sensor (TCG-3880). The size of the sample is restricted in this apparatus to 50 x 100 μm^2 fragments.

For the heat capacity measurements, an ac current is applied to the heater via a resistance in series and the corresponding temperature modulation is measured by the thermoelectric voltage output of the thermopile. It has been shown that helium gas acting as a heat exchange agent is ideal for utilizing this gauge for ac calorimetry. As shown by Minakov *et al.* (2005) [13], in the single thermal length limit and treating the heater as a point source, the heat capacity C is measured from the complex voltage of the thermopile and the Seebeck coefficient K of the membrane as defined in equation 1

$$V_{ac} = KP / (i\omega C + G) \quad (1)$$

where P is the heater power, ω is the frequency of temperature modulation and C includes the addenda contributions which have to be evaluated separately.

The alternative use of the gauge TCG-3880 is to employ it as a thermometer to measure the latent heat, analogous to the use of differential scanning calorimetry (DSC), as a function of field at constant temperature (see Miyoshi *et al.*, 2008) [14]. The helium exchange gas is used to set the measurement temperature before being pumped out to minimize the heat loss to the environment. Compared to other adiabatic methods the thin membrane minimizes the heat loss to the environment and also enables the measurement of small samples. The need for detailed characterization of the gauge as a thermometer, such as the temperature contour on the membrane, is circumvented by calibrating the measured thermoelectric voltage by sending an electrical pulse of known energy content to the heater circuit.

To extract the total entropy change ΔS_{total} between zero field and a finite field, as a function of temperature from calorimetry we use Eqs. (2)-(4). The entropy change from the equilibrium heat capacity values, ΔS_{HC} , is evaluated between T and T_1 , where T_1 is a reference temperature used for integration and is defined as the temperature at which ΔS_{total} is zero. ΔS_{LH} is the latent heat contribution, where ΔQ_L is the heat released by the material. As shown by Pecharsky *et al.*, (2001) [20], the total entropy change ΔS_{total} , is a sum of the two components ΔS_{HC} and ΔS_{LH} .

$$\Delta S_{HC}(T) = \int_T^{T_1} \frac{(C(H,T) - C(0,T))dT}{T} \quad (2)$$

$$\Delta S_{LH}(T) = -\frac{\Delta Q_L}{T} \quad (3)$$

$$\Delta S_{total}(T) = \Delta S_{HC}(T) + \Delta S_{LH}(T) \quad (4)$$

There has been some controversy concerning the evaluation of the entropy change with temperature from the magnetization (sometimes written as ΔS_M) for the first order phase transition, see for example, Giguère *et al.*, (1997) [19], Gschneidner *et al.*, (2000)[21], Sun *et al.*, (2000) [22] and Foldeaki *et al.*, (2000) [23]. In practice, it is observed that when the Maxwell relation (Eq. 5) is evaluated across the transition region only, Casanova *et al.* (2004) [24] it is in agreement with results obtained using the Clausius-Clapeyron relation (Eq. 6). In general, care should be taken when evaluating entropy changes, but here these concerns are less significant as we are able to determine the various contributions independently.

$$\Delta S_M(T, \Delta H) = \int_0^H \left(\frac{\partial M(T, H)}{\partial T} \right)_H dH \quad (5)$$

$$\Delta S_C = -\Delta M \frac{dH_c}{dT} \quad (6)$$

It should be noted that ΔS_{LH} relates to the contribution from the discontinuity in the free energy across the transition, the “first order contribution”, whereas ΔS_{HC} measures the change in equilibrium values of the heat capacity and is labelled the “second order contribution”. For systems that exhibit co-incident magnetic and structural transitions the interplay between a first order structural change and a second order magnetic transition can be complicated, depending on the relationship between the two transitions, see Jia *et al.*, (2006) [25], Bean and Rodbell (1962) [26]. Due to the sensitivity of a structural transition on pressure this has led to the investigation of the barocaloric properties of materials with respect to their magnetocaloric effects (de Medeiros (2008) [27]) and the suggestion of corrections to the mean field approach to account for such behavior (see Amaral *et al.*, 2007 [28], Plaza and Campoy (2007) [29]).

RESULTS

XRD showed that $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ powder crystallised in the orthorhombic perovskite structure (PBNM space group) with the lattice parameters $a=5.475(1) \text{ \AA}$, $b=5.459(2) \text{ \AA}$, $c=7.722(4) \text{ \AA}$, and unit cell volume = $230.82(12) \text{ \AA}^3$. The observed lattice parameters are close to those reported in the literature ($a=5.462 \text{ \AA}$, $b=5.452 \text{ \AA}$, $c=7.704 \text{ \AA}$) [30].

Figure 2. XRD pattern of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ powder calcined in air at 1150°C . HKL of several peaks are marked.

Magnetization and sweep rate dependence

Figure 3 (a) shows the magnetization versus field (M - H) loops taken at a magnetic field sweep rate of 0.5 T per minute. A significant sweep rate dependence to the hysteresis is observed, as shown in figure 3(b). Note that the relationship between sweep rate and hysteresis is non linear, but assuming that we can extrapolate back to zero sweep rate, it seems that the hysteresis is entirely extrinsic, in as much as it appears to approach zero at infinitely slow sweep rate. If we construct a phase line by defining the critical field H_c , as the position of the peak in the heat capacity with field curve (see fig 4(a)), we can correlate the extrinsic hysteresis at the maximum sweep rate, with a rise in sample temperature due to non isothermal conditions. Figure 3(c) shows the phase line defined this way which is quasi-linear, with a slope $dH_c/dT \sim 0.15 \text{ TK}^{-1}$. Using this plot we estimate that the sample temperature, which would give rise to the observed hysteresis is approximately 1K above the bath temperature. Fig 3(c) inset shows an Arrott plot, with signatures of S shaped curves usually taken to be indicative of a first order transition.

Figure 3. Shows (a) magnetization versus field (M - H) loops at 0.5 T per minute at a range of temperatures showing finite hysteresis, ΔH , defined as the separation between curves for different field sweep directions at the midpoint of the transition; (b) hysteresis width versus field sweep rate where lines on the graph are guide to the eye only; and (c) the critical field, H_c , versus temperature phase line, taken from the peak of the heat capacity curve with field (see fig 4(a)). Inset shows an H/M vs M^2 Arrott plot.

Calorimetry

Although the hysteresis appears to be extrinsic, there are systems which are very definitely first order, showing large latent heat peaks and small hysteresis. Hence in order to absolutely quantify the nature of the transition we performed calorimetric measurements. Figure 4 shows the results of ac heat capacity measurements. The field dependence of the heat capacity shows very large changes of the order of a 25% increase in the absolute value of heat capacity at the transition. The transition is therefore relatively well defined but the features are broad, and they broaden further as the transition moves out in field. The heat capacity was also measured as a function of temperature and we can clearly identify the zero field transition temperature. Using the adiabatic calorimetric method to capture latent heat as described above, we see absolutely no evidence for latent heat in this sample.

Figure 4. Shows (a) the ac heat capacity dependence on magnetic field for a selection of temperatures spanning 258K to 264K in 1K steps, and (b) the ac heat capacity dependence on temperature.

DISCUSSION

Mira et al., [31] claim that $\text{La}_{0.67}\text{Ca}_{0.33-x}\text{Sr}_x\text{MnO}_3$ shows a first order paramagnetic to ferromagnetic transition for $x = 0$ and $x = 0.1$. Here we study the $x = 0$ compound, and the entropy change of our sample, shown in figure 5(a) is directly compared and found to be similar to the previous Mira et al., report. Within error our sample appears to show precisely the same behavior in magnitude and temperature width to the literature performance. In a separate paper Ramos et al. [32] show that for $x = 0$ and 0.1, there is a relatively sharp volume change at the transition of the order of 0.05% (which is very small compared to the changes in lattice parameters of the order of 1% in LaFeSi and $\text{Gd}_5\text{Ge}_2\text{Si}_2$). We can calculate the entropy change using the magnetization curves or, from the ac calorimetry, and both are shown in figure 5(b). When a system has entropy change contributions from latent heat and a change of heat capacity both components have to be included in order for the total entropy change to equal that

calculated from the magnetization curves [33, 34]. In figure 5(b) it can be seen that the entropy change calculated from the ac calorimetry agrees with that calculated from magnetisation within the accuracy of our measurement which we estimate to be of the order of 1%. The minimum detectable signal using the calorimeter in its adiabatic temperature change mode for a sharp latent heat spike, is 0.01J/K/kg. For a maximum entropy change of ~ 3.5 J/K/kg (the data shown in figure 5), this is equivalent to 0.3% of the total entropy change. We see no evidence of a latent heat feature when we try to measure it, from which we infer that the very good match between the entropy change calculated from magnetization and ac calorimetry is unlikely to be fortuitous. If there is a missing latent heat contribution indicative of first order behavior then its total contribution to the entropy change can only be of the order of 0.3% or less. From which we conclude that if the sample is not entirely second order, then its first order character must be very weak indeed.

Figure 5. (a) Comparison to Mira et al., [27] (b) The entropy calculated from the magnetization or the heat capacity curves.

We do see hysteresis in the M-H loops, which could be attributable to intrinsic energy barriers and an indication of first order characteristics. However, on closer scrutiny, the hysteresis is sweep rate dependent and extrapolation to infinitely slow sweep rate suggests that the intrinsic hysteresis is zero. Previous authors have also commented on the zero hysteresis and the inconsistency with the expected first order behavior [35].

Several papers have commented on the missing entropy in manganites for example from localization of carriers at the ferromagnetic metal to paramagnetic insulator transition [36], or phase coexistence [36] or distributed transition due to the very specific dynamic Jahn Teller interaction that is thought to be present in these systems [37]. The entropy change simply assuming a local moment model of independent Mn spins can be estimated from $\Delta S_{\text{mn}} = R \ln(2S+1)$ where R is the gas constant and S is the spin state of the Mn ions. For $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ $\Delta S_{\text{mag}} = 0.67 \ln 5 + 0.33 \ln 4 = 12.8 \text{ Jmole}^{-1}\text{K}^{-1}$ and if the molecular weight of our compound is approximately 200g/mol, this converts to $\Delta S_{\text{mag}} \sim 64 \text{ JKg}^{-1}\text{K}^{-1}$. This model is likely to be far too simplistic in a system with electronic, spin and orbital ordering. Nevertheless as indicated by figure 5, it is clear that the entropy change we are capturing is far less than the simple model

would suggest. A more detailed statement concerning missing entropy is beyond the scope of this paper but the missing entropy question remains an intriguing one.

CONCLUSIONS

Manganites are proving to be an important candidate magnetic refrigerant system, in spite of rather low adiabatic temperature change in moderate fields (of the order of 2K), they are relatively inexpensive and can be made using well established solid state synthesis routes. They also lend themselves well to tunability in terms of the possibility to make graded material with a distribution of T_c values providing a good span of working temperatures, (many reviews have covered this detail previously). The most elusive aspect of the manganite system has been whether there is any clear evidence to support the claim that the ferromagnetic to paramagnetic transition is first order. We have investigated hysteresis, which may impact on use of these materials as refrigerants, in terms of thermal management as the manganites are known to have low thermal conductivity [12],[38-39] and this needs to be addressed. The system appears to show no intrinsic hysteresis. From calorimetric measurements and an attempt to measure any latent heat associated with the transition, we are unable to detect any direct evidence for first order behavior. Hence we conclude that the system is second order.

ACKNOWLEDGMENTS

This work was funded by the EPSRC grant number EP/G060940 “Nanostructured Functional Materials for Energy Efficient Refrigeration, Energy Harvesting and Production of Hydrogen from Water”.

REFERENCES

- [1] N Hirano et al., International Conference on Magnetic Refrigeration at Room Temperature, Thermag IV, Baotou, China August (2010).
- [2] Jun Shen, Yang-Xian Li, Feng-Xia Hu, and Ji-Rong Sun, *J. Appl. Phys.*, **105**, 07A901 (2009).
- [3] X.B. Liu, and Z. Altounian, *J. Magn. Magn. Mater.*, **264**, 209-213 (2003).
- [4] F.X. Hu, X.L. Qian, J.R. Sun, G.J. Wang, X.X. Zhang, Z.H. Cheng, and B.G. Shen, *J. Appl. Phys.*, **92**, 3620-3623 (2002).
- [5] A. Fujita, S. Fujieda, Y. Hasegawa, and K. Fukamichi, *Phys. Rev. B*, **67**, 104416, (2003).
- [6] J. Moore, K. Morrison, K.G. Sandeman, M. Katter, and L.F. Cohen, *Appl. Phys. Lett.* **95**, 252504(2009).
- [7] M.H. Phan, and S.C. Hu, *Phys. Stat. Sol.* **204**, 4091-4095 (2007).
- [8] V.K. Pecharsky and K.A. Gschneidner, Jr., *J. Appl. Phys.* **90**, 4614 (2001).
- [9] C. Ancona-Torres, N. Pryds, L.T. Kuhn, C.R.H. Bahl, and S. Linderöth, *J. Appl Phys.* **108**, 073914 (2010).
- [10] A.R. Dinesen, S. Linderöth, and S. Mørup, *J. Phys.: Condens. Matter* **17**, 6257-6269 (2005).
- [11] J. C. Loudon and P.A. Midgley, *Phys. Rev. Lett.* **96** 027214 (2006).
- [12] A.M. Aliev, A.B. Batdalov, and A.G. Gamzatov, *Low Temperature Physics* **36**, 171(2010).

- [13] A.A. Minakov, S.B. Roy, Y.V. Bugoslavsky, and L.F. Cohen, *Rev. Sci. Instr.* **76**, 043906 (2005).
- [14] Y. Miyoshi, K. Morrison, J.D. Moore, A.D. Caplin, and L.F. Cohen, *Rev. Sci. Instr.* **79**, 074901 (2008).
- [15] G.K. Perkins, J.D. Moore, M.K. Chattopadhyay, S.B. Roy, P. Chaddah, V.K. Pecharsky, K.A. Gschneidner, and L.F. Cohen, *J. Phys. Condens. Matt.* **19**, 176213 (2007).
- [16] M.D. Kuz'min, and M. Richter, *Phys. Rev. B* **76**, 092401 (2007).
- [17] J. D. Moore, G. K. Perkins, Y. Bugoslavsky, M. K. Chattopadhyay, S. B. Roy, P. Chaddah, V.K. Pecharsky, K. A. Gschneidner, Jr., and L. F. Cohen, *Appl. Phys. Lett.* **88**, 072501 (2006).
- [18] T.J.B. Holland, and S.A.T. Redford, *Mineralog. Mag.* **61**, 65(1997).
- [19] A.Giguère, M. Foldeaki, B.R. Gopal, R. Chahine, T.K. Bose, A. Frydman, and J.A. Barclay, *Phys. Rev. Lett.* **83**, 2262 (1999).
- [20] V.K. Pecharsky, K.A. Gschneidner, Jr., A.O. Pecharsky, and A.M. Tishin, *Phys. Rev. B* **64**, 144406 (2001).
- [21] K.A. Gschneidner, Jr., V.K. Pecharsky, E. Brück, H.G.M. Duijn, and E.M. Levin, *Phys. Rev. Lett.* **85**, 4190 (2000).
- [22] J.R. Sun, F.X. Hu, and B.G. Shen, *Phys. Rev. Lett.* **85**, 4191 (2000).
- [23] M. Foldeaki, R. Chahine, T.K. Bose, and J.A. Barclay, *Phys. Rev. Lett.* **85** 4192 (2000).
- [24] F. Casanova, A. Labarta, X. Batlle, J. Marcos, L. Manosa, A. Planes, and S. de Brion, *Phys. Rev. B* **69**, 104416 (2004).
- [25] L. Jia, G.J. Liu, J.R. Sun, H.W. Zhang, F.X. Hu, C. Dong, G.H. Rao, and B.G. Shen, *J. Appl. Phys.* **100**, 123904 (2006).
- [26] C.P. Bean, and D.S. Rodbell, *Phys. Rev.* **126**, 104 (1962).
- [27] L.G. de Medeiros, Jr, N.A. de Oliveira, and A. Troper, *J. Appl. Phys.* **103**, 113909 (2008).
- [28] J.S. Amaral, N.J.O. Silva, and V.S. Amaral, *Appl. Phys. Lett.* **91**, 172503 (2007).
- [29] E.J.R. Plaza, and J.C.P. Campoy, *Phys. Rev. B* **75**, 174419 (2007).
- [30] P.G. Radaelli, D.E. Cox, M. Marezio, and S.W. Cheong, *Phys. Rev. B*, **55**, 3015 (1997).
- [31] J. Mira, J. Rivas, L.E. Hueso, F. Rivadulla, and M.A. López Quintela, *J. Appl. Phys.*, **91**, 8903 (2002).
- [32] C.A. Ramos, H.R. Salva, R.D. Sanchez, M. Tovar, F. Rivadulla, J. Mira, J. Rivas, A.M. Lopez-Quintela, L. Hueso, M. Saint-Paul, P. Lejay, and Y. Tokura, *J. Magn. Magn. Mater.* **226-230**, 582-584 (2001).
- [33] K. Morrison, J.D. Moore, K.G. Sandeman, A.D. Caplin, and L.F. Cohen, *Phys. Rev. B* **79**, 134408 (2009).
- [34] K. Morrison, J. Lyubina, J.D. Moore, A.D. Caplin, K.G. Sandeman, O. Gutfleisch, and L.F. Cohen, *J. Phys. D: Appl. Phys.* **43**, 132001 (2010).
- [35] M.R. Lees, O.A. Petrenko, G. Balakrishnan, and D.M. Paul, *Phys. Rev. B* **59**, 1298 (1999).
- [36] A.P. Ramirez, P. Schiffer, S.W. Cheong, C.H. Chen, W. Bao, T.T.M. Palstra, P.L. Gammel, D.J. Bishop, and B. Zegarski, *Phys. Rev. Lett.* **76**, 3188 (1996).
- [37] J.M. De Teresa, M.R. Ibarra, P. Algarabel, L. Morellon, B. Garcia-Landa, C. Marquina, C. Ritter, A. Maignan, C. Martin, B. Raveau, A. Kurbakov, and V. Trounov, *Phys. Rev. B* **65**, 100403 (2002).
- [38] D.W. Visser, A.P. Ramirez, and M.A. Subramanian, *Phys. Rev. Lett.* **78**, 3947 (1997).
- [39] J. Liebe, E. Kraus, L. Haupt, P. Mandal, K. Barner, and R. vonHelmolt, *Appl. Phys. Lett.* **68**, 2343 (1996).