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*Published in:*  
Journal of Magnetism and Magnetic Materials

*Link to article, DOI:*  
[10.1016/j.jmmm.2016.05.011](https://doi.org/10.1016/j.jmmm.2016.05.011)

*Publication date:*  
2016

*Document Version*  
Peer reviewed version

[Link back to DTU Orbit](#)

*Citation (APA):*  
Neves Bez, H., Nielsen, K. K., Smith, A., & Bahl, C. R. H. (2016). A detailed study of the hysteresis in  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ . *Journal of Magnetism and Magnetic Materials*, 416, 429-433.  
<https://doi.org/10.1016/j.jmmm.2016.05.011>

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# A detailed study of the hysteresis in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$

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## Abstract

We report a thorough study of the thermal hysteretic behaviour of a single phase sample of the magnetocaloric material  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ . Previous reports in the literature have variously found hysteretic and non-hysteretic behaviour. We show the importance of measuring under carefully defined heating and cooling procedures. Careful analysis of the specific heat, measured at five different temperature ramp rates, and the magnetic entropy change indicates that there is no observable hysteresis, even though the behaviour of both quantities is consistent with a first-order phase transition. We discuss the reasons for this and for the differing results previously found.

*Keywords:* Magnetocaloric effect, Hysteresis, Phase transition, Manganites

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## 1. Introduction

A broad range of materials display the magnetocaloric effect. An interesting example is the Lmanganites, in particular  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  which has been investigated for several years as a possible material for magnetocaloric applications [1, 2, 3]. Of particular interest is whether the phase transition is of first order or of second order. As a general rule, materials with a first-order phase transition (FOPT) can exhibit a larger magnetocaloric effect than materials with a second-order phase transition (SOPT). On the other hand thermal hysteresis, which gives rise to losses when the materials are applied in thermodynamic cycles, is associated with FOPT. This makes it of both theoretical and practical importance to investigate the hysteresis of magnetocaloric materials.

$\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  has been the subject of much research over the past decades due to its many interesting properties. Even so, it remains a much debated question whether the material undergoes a FOPT or a SOPT [4, 5]. Furthermore, thermal hysteresis has been studied in this material with contradicting results [1, 5, 6, 7]. One complication is that different processing routes may lead to dif-

ferent properties [8], e.g. the reported Curie temperatures vary between 250 to 270 K. Furthermore, care has to be taken when investigating thermal hysteresis in FOPT to avoid sampling metastable mixed states in the transition region between the paramagnetic and ferromagnetic states. It has previously been shown that for observation of the true thermal hysteresis it is necessary to ‘reset’ the sample between measurements by cooling or heating to a temperature where only one phase is present [9, 10].

One of the models used to shed some light on the magnetic phase transition of materials is the Bean-Rodbell model [11]. Bean and Rodbell have proposed that the exchange constant, and therefore  $T_C$ , varies linearly with the lattice spacing as  $T_C = T_0[1 + \beta \frac{V - V_0}{V_0}]$ , where  $V$  is the unit cell volume,  $T$  is temperature, and  $T_0$  and  $V_0$  are temperature and unit cell volume in the absence of exchange interaction, respectively. The parameter denoted by  $\beta$  controls the strength of the spin-lattice coupling. Moreover, one of the implications of this model is the introduction of possible irreversibilities, such as hysteresis. One of the parameters of the model,  $\eta$ , can control whether the transition is first order,  $\eta > 1$ , or second order,  $\eta \leq 1$ . This model has been used with good agreement with measured properties of some compositions of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ , where it was observed  $\eta$  values

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55 above 1 [12], i.e. first order phase transition. Furthermore, literature has shown that by superimposing a Gaussian distribution in the Curie temperature, one can simulate the effect of chemical inhomogeneities on the properties [13].

60 Here we use measurements of  $c_p$  and both indirect and direct measurements of the isothermal entropy change  $\Delta s$  to evaluate the phase transition of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ . The indirect measurement is done by measuring the magnetization as a function of field and temperature and subsequently using a numerical integration of the Maxwell relation  $\Delta s = \mu_0 \int (\partial M / \partial T) dH$ , while the direct measurement uses calorimetry [14, 15, 16]. The latter avoids the approximations arising from the numerical integration and provides a very stable temperature for the measurements. Below we report studies of the thermal hysteretic and FOPT behaviour by means of measurements of  $\Delta s$  and  $c_p$ , and by the implementation of Bean-Rodbell model of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  produced by solid-state reaction.

## 2. Experimental Procedure

80  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  polycrystalline material was synthesized by solid-state reaction.  $\text{La}_2\text{O}_3$ ,  $\text{CaCO}_3$  and  $\text{MnO}_2$  in powder form were ground and mixed stoichiometrically by roll milling during 48 h with a rotation speed of 180 rpm. The powder was then calcinated at 1123 K for 24 h. Subsequently, the powder was isostatically pressed into pellets and sintered at 1403 K for 48 h. Both calcination and sintering were performed in air. X-ray diffraction (XRD) measurements were performed in a Bruker D8 X-ray diffractometer at ambient temperature and pressure, under Cu radiation. The specific heat,  $c_p$ , was measured at different temperature rates in a custom-built differential scanning calorimeter (DSC) [17] under several applied fields. The isothermal entropy change was measured for every 0.25 K in the same device, by keeping the temperature fixed and varying the applied magnetic field. We used four different measurement protocols around the transition temperature to avoid the appearance of mixed states when characterizing the entropy change:

- 100 i. From the ferromagnetic state (FM) towards paramagnetic state (PM) with a reset temperature at 240 K and going from 0 T to 1.0 T;

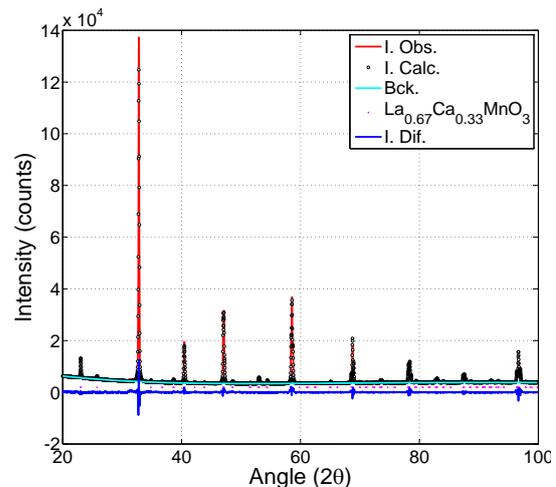


Figure 1: XRD pattern and Rietveld refinement of the perovskite showing the desired single phase structure.

- ii. From FM towards PM with a reset temperature at 240 K and going from 1.0 T to 0 T;
- iii. From PM towards FM with a reset temperature at 290 K and going from 0 T to 1.0 T;
- iv. From PM towards FM with a reset temperature at 290 K and going from 1.0 T to 0 T;

When resetting, the sample is taken to the chosen reset temperature and allowed to thermally equilibrate. Low temperature magnetisation was measured in a high field VSM (Cryogen Free Measurement System - 16 T) at 10 K from 0 to 10 T, with a rate of 0.1 T/min to find the saturation magnetisation. Moreover, a LakeShore VSM, model 7407, was used to measure isothermal magnetisation around the transition temperature in order to calculate  $\Delta s$ , and compare with the direct measurements in the calorimeter. These  $\Delta s$  measurements were done from 0 T to 1.6 T and for every 0.5 K. The demagnetization effects were taken into account when processing the data, assuming a prism shaped sample [18]. The sample has the approximate dimensions  $3.8 \times 1.2 \times 1.2 \text{ mm}^3$ . The field orientation in the isothermal magnetization measurements was along the long axis to minimize demagnetization, while in the DSC the field was along the short axis, due to size incompatibility.

## 3. Results

LCMO has an O-type orthorhombic structure, with a distortion of the  $\text{MnO}_6$  octahedra due to the Jahn-Teller effect [19]. Figure 1 shows the XRD

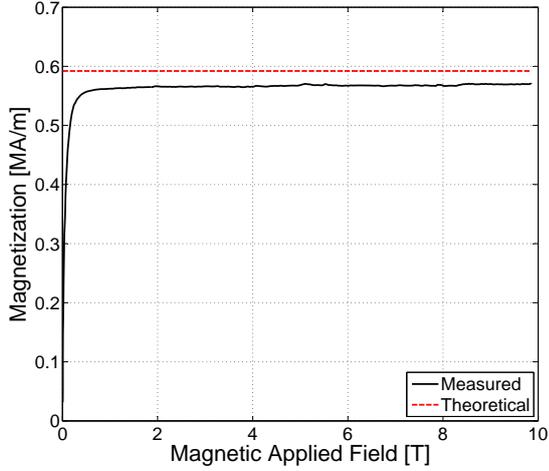


Figure 2: Magnetisation measurement at 10 K, from 0 T to 10 T at a rate of 0.1 T/min. The solid line represents the measurement, and the dashed red line is the theoretical value of the saturation magnetisation.

pattern and Rietveld refinement of the polycrystalline  $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$ . From the Rietveld refinement one may observe the single phase pattern of  $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$  where the unit cell parameters  $a$ ,  $b$  and  $c$  were calculated to be 5.47154(7) Å, 5.45690(1) Å and 7.7086(1) Å, respectively, resulting in a unit cell with a volume of 230.162(7) Å<sup>3</sup>, which is in agreement with the literature [4]. Furthermore, Figure 2 shows the magnetisation measurement at 10 K, where the solid line is the measurement and the dashed red line is the theoretical saturation value calculated as follows:

$$M_s = g\mu_B J \rho_s. \quad (1)$$

Here,  $g$  is the Landé factor,  $\mu_B$  is the Bohr magneton,  $J$  is the total quantum angular momentum and  $\rho_s$  is the magnetic spin density. The Landé factor used is 2,  $J$  is 1.835 (average on the ratio of  $\text{Mn}^{+3}$  and  $\text{Mn}^{+4}$ ) and the spin density is calculated simply by the number of magnetic atoms (four) in the volume  $V$  obtained by XRD, giving a magnetic spin density of  $1.7391\text{e}28$  spins/m<sup>3</sup>. These values were used to calculate the theoretical saturation magnetization. One can see that the experimental and theoretical values are in good agreement; the measured magnetisation value,  $3.57 \mu_B$  per unit formula, is around 97% of the theoretical saturation magnetisation value,  $3.67 \mu_B$  per unit formula.

In order to evaluate the specific heat under heating and cooling conditions, it was measured for different temperature rates, Fig. 3. The peak val-

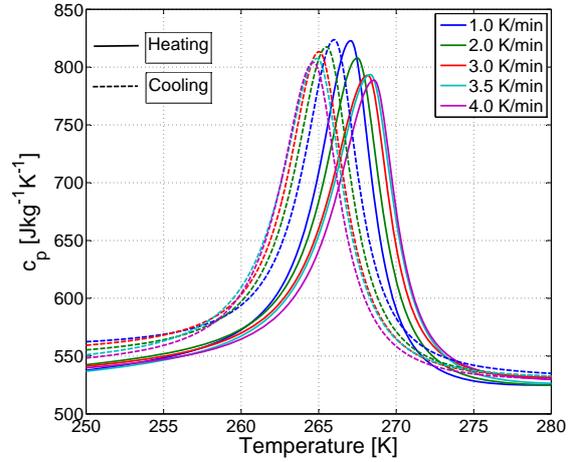


Figure 3: Specific heat as a function of temperature for different temperature rates at 0 T.

ues and positions are in agreement with the literature [1, 5]. The peak temperatures ( $T_{\text{peak}}$ ) of the  $c_p$  curves were fitted as a function of rate in order to exclude the extrinsic hysteresis, as shown in Fig. 4. The observed hysteresis decreases with decreasing temperature rates, and for the extrapolated 0 K/min rate, the intrinsic hysteresis is 0.08 K, virtually zero considering the fitting and extrapolation uncertainties,  $\pm 0.2$  K. It is interesting to notice that the expected  $\Delta T_{\text{hyst}}$  for a rate of 5 K/min, is the same as the one reported elsewhere [1].

The extrinsic hysteresis under different temperature rates is related to the thermal diffusivity of the material.  $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$  has a large specific heat and a relatively low thermal conductivity,  $1\text{-}3 \text{ Wm}^{-1}\text{K}^{-1}$  [20], which then leads to a low thermal diffusivity. Considering the base level of  $c_p = 550 \text{ Jkg}^{-1}\text{K}^{-1}$ , the density obtained from the XRD measurement  $\rho = 6034 \text{ kgm}^{-3}$  and assuming a value of  $\kappa = 2 \text{ Wm}^{-1}\text{K}^{-1}$ , the thermal diffusivity can be calculated by  $D = \kappa/c_p\rho$  and for  $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$  it is  $6 \cdot 10^{-7} \text{ m}^2\text{s}^{-1}$ . This is approximately five times smaller than other common magnetocaloric materials such as  $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$  where it is  $\sim 2.7 \cdot 10^{-6} \text{ m}^2\text{s}^{-1}$ , very similar to the diffusivity of Gd [21]. Therefore, the temperature rate is much more influential on the position of the peaks of  $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$  compared to other magnetocaloric materials.

To further investigate the thermal hysteresis, specific heat measurements under different applied fields were performed. Figure 5 shows the heat ca-

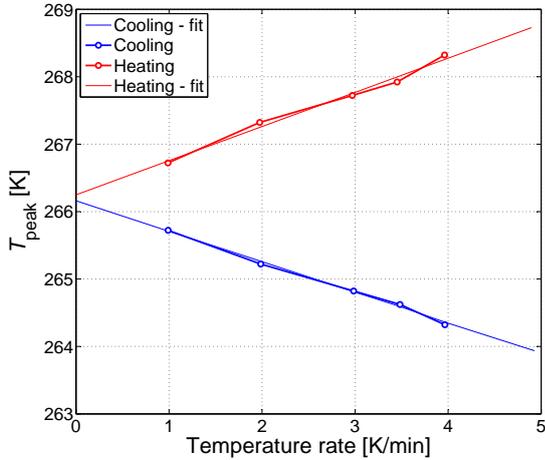


Figure 4: Heat capacity peak temperature,  $T_{\text{peak}}$ , as a function of temperature rates for both heating and cooling. At finite heating and cooling rates extrinsic hysteresis is apparent. However, the intrinsic hysteresis, corresponding to the extrapolated temperature rate 0 K/min, vanishes.

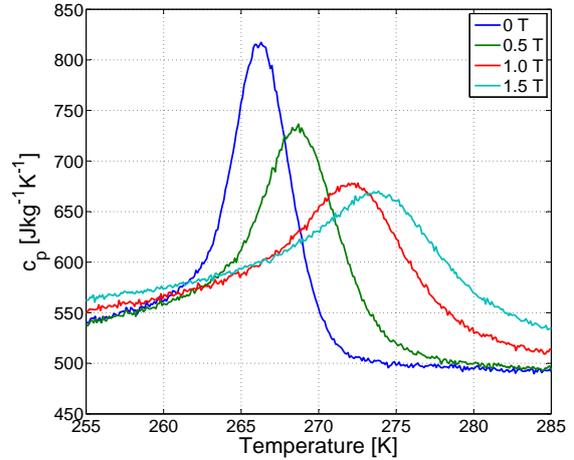


Figure 5: Specific heat as a function of temperature and under different applied field, with  $\dot{T} = -1.0$  K/min.

195 capacity during the cooling procedure with  $\dot{T} = -1.0$   
 K/min, under different applied fields. As the graph  
 shows, the heat capacity peak is shifting towards  
 higher temperatures for increasing values of  $H$ .  
 This indicates a behaviour similar to that of a first  
 order phase transition [22]. Figure 6 shows  $T_{\text{peak}}$   
 200 as a function of field, for both heating and cooling pro-  
 cedures, with  $|\dot{T}| = 1.0$  K/min. The linear fits show  
 a slope of  $6.2 \pm 0.9$  K/T for both the heating and  
 cooling procedures. Furthermore, when extrapolat-  
 205 ing to a rate of 0 K/min as in Figure 4, the lines col-  
 lapse showing the absence of hysteresis. In contrast,  
 for materials with intrinsic hysteresis the amount of  
 hysteresis decreases linearly with field, until a criti-  
 cal field is reached at which the transition becomes  
 210 continuous and there is no more hysteresis.

Figure 7 shows indirect measurements of  $\Delta s$  as  
 a function of temperature for different values of  
 $\Delta H$ . One may see the asymmetric behaviour of  
 the peak with increase in field; a behaviour related  
 215 to first order transitions [22]. A slight hysteretic be-  
 haviour around the  $T_{\text{peak}}$  is observed, with a  $\Delta T_{\text{hyst}}$   
 of approximately 0.7 K in the full-width half max-  
 imum (FWHM). On the other hand, direct mea-  
 220 surements of  $\Delta s$  (see Figure 8) show no observable  
 difference between the peak positions and, there-  
 fore, no significant thermal hysteresis was observed.  
 The peak value is in agreement with literature val-  
 ues [5]. The difference between the two types of  
 measurements arises from the uncertainties related

225 to the measurements. As Pecharsky and Gschnei-  
 dner [23] have shown,  $\Delta s$  derived from magnetisa-  
 tion measurements may have an uncertainty of up  
 to 20%, making it challenging to try to extract reli-  
 230 able values of a small or non-existent hysteresis. It  
 is important to note that the direct measurement of  
 $\Delta s$ , is done with a high precision instrument with a  
 temperature uncertainty of  $\pm 10$ mK [16]. Further-  
 235 more, each point is measured individually, avoiding  
 the smoothing effect observed when finite difference  
 approximation is used to calculate  $\Delta s$  from mag-  
 netisation derivatives.

#### 4. Discussion

We find no discernible *apparent* hysteresis in  
 LCMO, as shown above through the measurements  
 of heat capacity and calorimetric measurements of  
 entropy change. This is consistent with previous re-  
 ports using an AC calorimetric method [5]. On the  
 other hand the observed behaviour of the specific  
 heat and isothermal entropy change is characteris-  
 245 tic of a FOPT. These observations can be recon-  
 ciled if we consider the spread in critical temper-  
 ature which is caused by compositional variations  
 and the tendency to formation of magnetically in-  
 homogeneous states in the manganites [13]. For  
 weakly first-order materials even a small spread in  
 critical temperatures may be enough to smooth out  
 the transition and make the hysteresis disappear.  
 Recently we showed, using detailed determination  
 of the field dependence of  $\Delta s$  at  $T_c$  in combina-

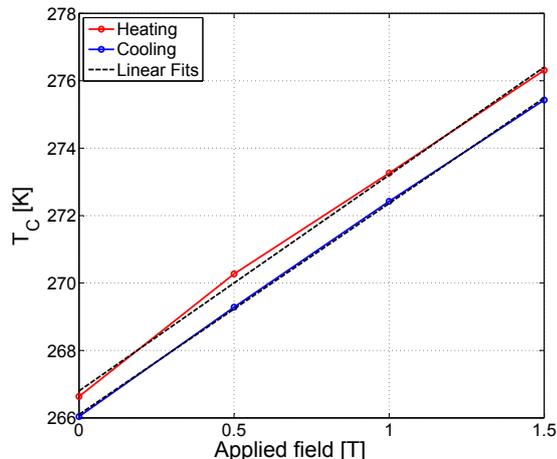


Figure 6: The specific heat peak temperature,  $T_{\text{peak}}$ , as a function of applied magnetic fields for both heating and cooling heat capacity measurements, with  $|\dot{T}| = 1.0$  K/min. The dashed lines are linear fits.

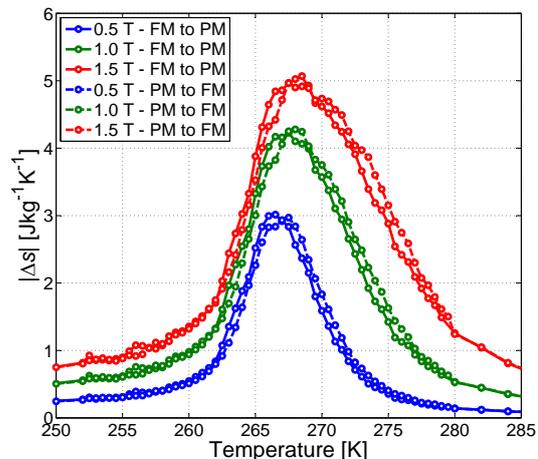


Figure 7: Entropy change calculated from magnetisation measurements from the VSM, using method (i) and (iii), from 0 T to 0.5, 1.0 and 1.5 T.

tion with a fit to the Bean-Rodbell model that it is possible to determine the order of the phase transition and the spread in critical temperature [24]. We find indeed that  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  is weakly first order, with an  $\eta = 1.25$ . In Figure 9 we show the modelled behaviour of the entropy curve under both heating and cooling, with a standard deviation on the Gaussian distribution  $\sigma(T_0) = 2.6$  K, and without any distribution. It is clear that the weak hysteresis present when there is no compositional inhomogeneity, i.e.  $\sigma(T_0) = 0$  K, tends to vanish when the spread is taken into consideration, i.e.  $\sigma(T_0) = 2.6$  K. It is also important to notice that the entropy curve shown here is in zero field. Previous works [22, 25] have shown that the thermal hysteresis decreases with the increase of magnetic field, making it the largest at zero field. Moreover, the inset shows the entropy change under heating and cooling procedures, for both distributions and a magnetic field change of 1 T. One may see the great impact that the spread causes in the entropy change, making the peak wider and smaller. We have seen the same behaviour recently [26] in  $\text{La}(\text{Fe}, \text{Mn}, \text{Si})_{13}\text{H}_y$ . We believe such behaviour is due to the chemical inhomogeneity. If a material with mass  $m$  has a single  $T_C$ , all its mass will undergo the transition at that temperature, concentrating all the entropy change at it. However, if the material has a distribution in  $T_C$  due to, e.g., chemical inhomogeneity, different parts of the material will change from FM to PM at different temper-

atures, so the entropy change will be distributed accordingly to the distribution of  $T_C$ .

## 5. Conclusions

We have studied the thermal hysteretic behaviour of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  by means of several measurements and modelling. Direct  $\Delta s$  measurements with 0.25 K step, measured in 4 different setups have shown no temperature difference. Heat capacity measured under 0 T and different temperature rates have shown no hysteresis when done the extrapolation to equilibrium state. Observed hysteresis does not decrease with field, pointing to the absence of intrinsic hysteresis. Still, FOPT behaviour was observed as  $c_p$  shifting with field and the asymmetric growth of  $\Delta s$  with increasing field changes. FOPT modelled with Bean-Rodbell model and with a superimposed Gaussian distribution on the  $T_C$  have shown that the spread in  $T_C$  can decrease significantly, or even vanish the hysteresis.

## 6. Acknowledgements

This work was financed by the ENOVHEAT project which is funded by Innovation Fund Denmark (contract no 12-132673).

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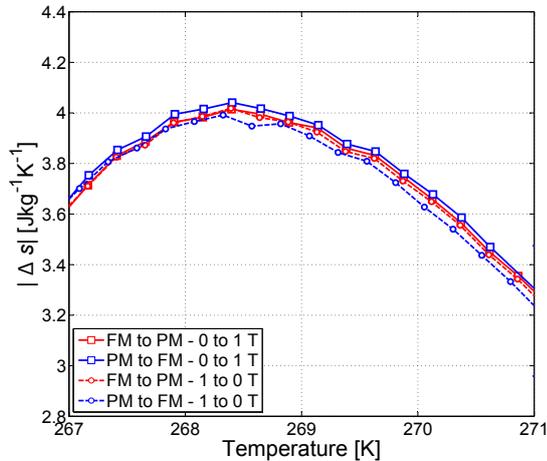


Figure 8: Entropy change measured directly in the DSC, around the transition temperature with a temperature step of 0.25 K.

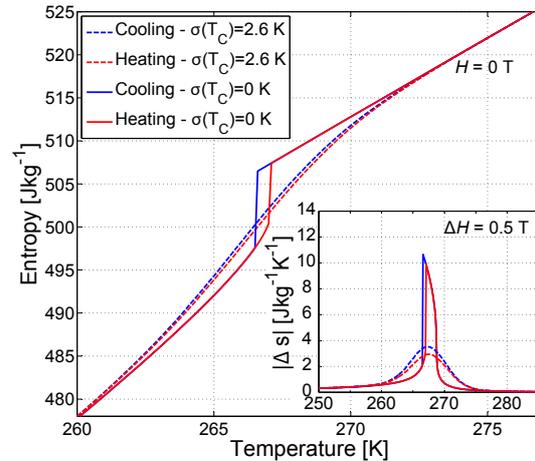


Figure 9: Entropy as function of the temperature, for heating and cooling procedures, and  $H = 0$  T. One may see the vanishing impact of the distribution  $\sigma(T_C)$  on the hysteresis. The inset shows the modelled isothermal entropy change for  $\Delta H = 0.5$  T, during heating and cooling procedures.

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