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Estimating spontaneous magnetization from a mean field analysis of the magnetic entropy change

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ABSTRACT

The magnetocaloric effect is a common property of all magnetic systems, corresponding to a temperature change under adiabatic conditions (ΔT_{ad}) or a change in magnetic entropy in isothermal conditions (ΔS_M), for a given applied magnetic field change. ΔT_{ad} can be directly measured under adiabatic conditions and indirectly estimated from specific heat measurements. ΔS_M can be indirectly estimated from specific heat measurements or magnetization measurements (the usual approach). Early work on the study of ferromagnets used direct measurements of ΔT_{ad} to determine the spontaneous magnetization for a given temperature value. In this work, we use ΔS_M obtained from isothermal magnetization measurements to estimate the spontaneous magnetization, comparing this result to mean-field fittings from a novel scaling method, discussing the validity and usefulness of this approach from considerations from the Landau theory of phase transitions.

1. Introduction

The magnetocaloric effect, discovered by Warburg in 1881 [1], is a common property of all magnetic systems and is induced via coupling of the system of atomic magnetic moments with the magnetic field, which alters the magnetic part of the total entropy due to a corresponding change of the magnetic field. Under adiabatic conditions, this leads to a temperature change, or to heat exchange under isothermal conditions. This effect is behind magnetic cooling, an efficient and ecologically friendly alternative to vapor-based refrigeration technologies [2–4].

Significant advances have been made in interpreting the magnetocaloric properties of materials. The use of phenomenological theories has given us valuable insight in this matter. Landau theory has allowed us to assess the importance of magnetoelastic coupling in the magnetocaloric effect [5,6]. Mean-field theory has established direct relations between magnetic entropy change and magnetization [4,7,8]. The theory of critical phenomena justifies the existence of a universal magnetocaloric behavior in second-order magnetic phase transition materials [9,10].

Early work on the study of the spontaneous magnetization of ferromagnets [11], consisted on directly measuring the adiabatic temperature change ΔT_{ad} of a material, since within a molecular field approach the relation between ΔT_{ad} and the spontaneous magnetization is established. For a general presentation, see Refs. [12,13]. The use of Landau theory and the Arrott plot construction [14] is also a convenient way to estimate spontaneous magnetization.

In this work, isothermal magnetic entropy change (ΔS_M) values of second- and a first-order ferromagnetic manganite systems, taken from isothermal magnetization measurements, are used much in the same way as ΔT_{ad} measurements, to estimate the spontaneous magnetization of these systems. The results of this approach are compared to the results from a generalized mean-field analysis [15] that successfully reproduced the magnetic properties of both the second- and first-order systems, within a broad temperature range.

2. Theoretical background and methodology

A general result from mean-field theory is that magnetic entropy $S(\sigma)$ can be described as [4,7,8]:

$$S(\sigma) = -Nk_B\left[\ln(2J+1) - \ln\left(\frac{\sinh\left(\frac{2J+1}{2J}B^{-1}(\sigma)\right)}{\sinh\left(\frac{1}{2J}B^{-1}(\sigma)\right)}\right) + B^{-1}(\sigma).\sigma\right] \quad (1)$$

where N is the number of spins, J the spin value, k_B the Boltzmann constant, σ the reduced magnetization and B_J the Brillouin function for a given J value.

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From a power expansion of Eq. (1), ΔS_M is proportional to M^2, from the mean-field model, for small M values:

$$-S(\sigma)=\frac{3}{2}\frac{J}{J+1}Nk_B\sigma^2+O(\sigma^4). \tag{2}$$

This result is in agreement with Landau theory, where estimating the entropy from the temperature derivative of the Gibbs free energy expansion [5] results in

$$-S_M(T,H)=\left(\frac{\partial G}{\partial T}\right)_H=\frac{1}{2}A'M^2+\frac{1}{4}B'M^4+\frac{1}{6}C'M^6, \tag{3}$$

where A', B', C' are the temperature derivative of the Landau expansion coefficients, and M the magnetization value obtained from the minimization of the free energy expansion.

The first term of the expansion is temperature independent and is equal to 1/2 of the inverse Curie constant for both models (Eqs. (2) and (3)). In the ferromagnetic state the system has a spontaneous magnetization and the $\sigma=0$ state is never attained. Explicitly, and considering only the first term of the expansion of Eq. (2), this corresponds to

$$-\Delta S(\sigma)=\frac{3}{2}\frac{J}{J+1}Nk_B(\sigma^2-\sigma^2_{\mathrm{spont}}), \tag{4}$$

which results in a shift of the isothermal ΔS_M vs M^2 plots in the ferromagnetic region, with an horizontal drift from the origin corresponding to the value of $M^2_{\mathrm{spont}}(T)$, while for $T>T_C$ the ΔS_M vs M^2 plots start at a null M value.

From bulk isothermal magnetization measurements, ΔS_M values are calculated directly from the use of a Maxwell relation:

$$\left(\frac{\partial S}{\partial H}\right)_T=\left(\frac{\partial M}{\partial T}\right)_H, \tag{5}$$

and a suitable numerical approximation:

$$|\Delta S_M|=\int\left(\frac{\partial M}{\partial T}\right)dH\simeq\sum\frac{(M_n-M_{n+1})_H}{T_{n+1}-T_n}\Delta H_n. \tag{6}$$

If the ΔS_M vs M^2 plots show a linear dependence with constant slope throughout the experimental temperature/field range, this corresponds to the validity of the linear expansion of Eq. (4), or, in Landau theory, to temperature independent B and C parameters (Eq. (3)). We therefore have the basis to determine the spontaneous magnetization of materials from isothermal ΔS_M vs M^2 plots, from linear fits inside the ferromagnetic region.

We have used this methodology for two manganite systems, the second-order $La_{0.665}Eu_{0.035}Sr_{0.30}MnO_3$ and the first-order $La_{0.638}Eu_{0.032}Ca_{0.33}MnO_3$.

3. Second-order phase transition manganite

From magnetization and ΔS_M data of the $La_{0.665}Eu_{0.035}Sr_{0.30}MnO_3$ system, taken from our Ref. [6], the ΔS_M vs. M^2 plot is constructed, as shown in Fig. 1.

Clear areas of a linear dependence of ΔS_M on M^2 are visible, with an approximately constant slope throughout the ferromagnetic region. Due to the formation of magnetic domains, the plots tend to a zero spontaneous magnetization value at the ferromagnetic region, but this effect can be confidently surpassed by extrapolating the linear regime, as shown. The obtained slope from ΔS_M on M^2 plots is approximately 29.4 (cgs), corresponding to a Curie constant of 0.0170 (emu K Oe^{-1} g^{-1}), from Eq. (4). The

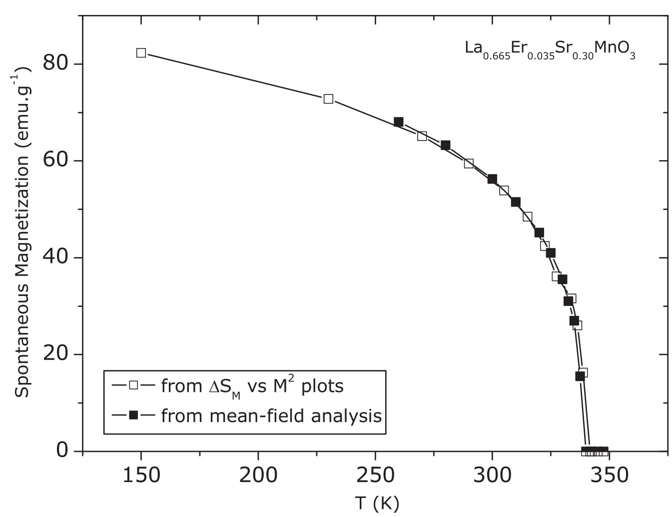

Fig. 2. Spontaneous magnetization of $La_{0.665}Eu_{0.035}Sr_{0.30}MnO_3$, estimated from extrapolating the ΔS_M vs. M^2 curves of Fig. 1 (open squares), and from the mean-field results of Ref. [16] (closed squares). Lines are eye-guides.

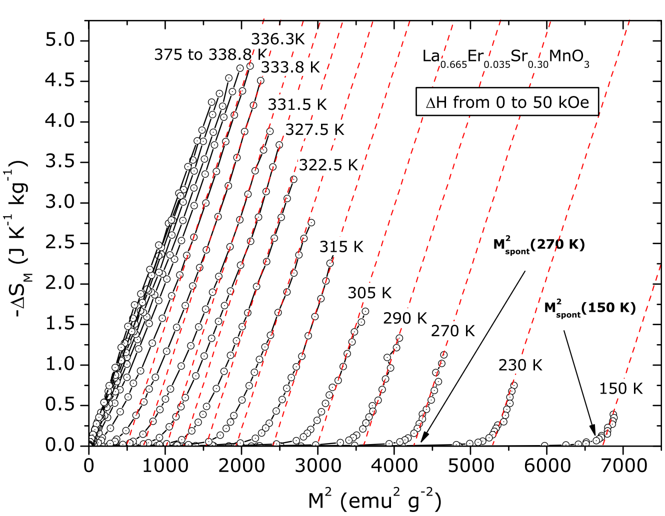

Fig. 1. (Color online) Isothermal ΔS_M vs. M^2 curves of $La_{0.665}Eu_{0.035}Sr_{0.30}MnO_3$ and an applied field change from 0 to 50 kOe. Dashed lines represent constant slope linear fits to data, that extrapolate to the square of the spontaneous magnetization values for $T<T_C$ isotherms, as explicitly shown for two representative isotherms.

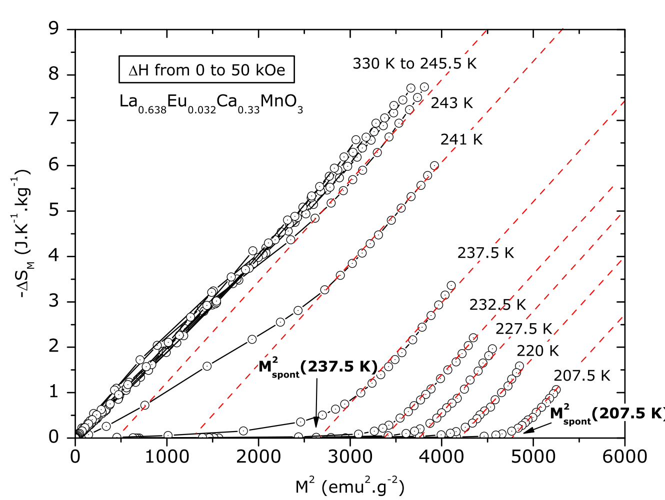

Fig. 3. (Color online) Isothermal ΔS_M vs. M^2 curves of $La_{0.638}Eu_{0.032}Ca_{0.33}MnO_3$ and an applied field change from 0 to 50 kOe. Dashed lines represent constant slope linear fits to data, that extrapolate to the square of the spontaneous magnetization values for $T<T_C$ isotherms, as explicitly shown for two representative isotherms.

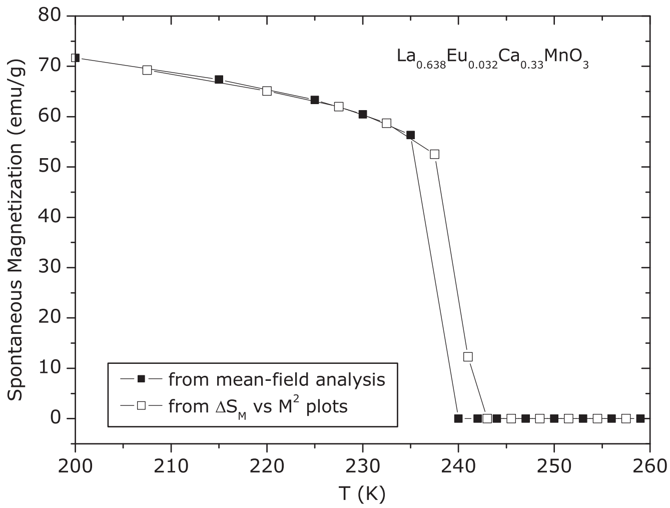

Fig. 4. Spontaneous magnetization of $La_{0.638}Eu_{0.032}Ca_{0.33}MnO_3$, estimated from extrapolating the ΔS_M vs. M^2 curves of Fig. 3 (open circles), and from the mean-field results of Ref. [15] (closed squares). Lines are eye-guides.

spontaneous magnetization is then estimated, and compared to the results from the mean-field analysis of Ref. [16], as shown in Fig. 2.

A good agreement between methods is obtained. While our detailed analysis of magnetization data with the molecular mean-field model uses a scaling approach, estimating the spontaneous magnetization from ΔS_M vs. M^2 is a quite simpler process. The fitting procedure is also simpler compared to an analysis of Arrott plots, since only the explicit derivative of the Landau coefficients is considered, as discussed in Section 2. For this system in particular, B' and C' are negligible.

4. First-order phase transition manganite

The same methodology is used for the study of the first-order phase transition manganite $La_{0.638}Eu_{0.032}Ca_{0.33}MnO_3$. From experimental magnetization data from Ref. [15], the ΔS_M vs. M^2 curves are calculated (shown in Fig. 3). Much like the results of the second-order manganite (Fig. 1), there is a clear linear dependence of magnetic entropy change on the square of magnetization, apart from the region of data where magnetic domains are present.

For this system, the linear regions of the ΔS_M vs. M^2 plots show a temperature-independent slope, approximately 22.4 (cgs), which corresponds to a Curie constant value of 0.0223 (emu K Oe^{-1} g^{-1}), from Eq. (4).

The spontaneous magnetization results as a function of temperature are shown in Fig. 4.

The sharp increase of spontaneous magnetization, characteristic of a first-order magnetic phase transition, is reproduced with both methods, where a small shift of ~ 2 K is observed, which is within the experimental temperature step of measurements.

5. Conclusions

In this work we have verified the agreement between two different methodologies of determining the spontaneous magnetization from bulk magnetization measurements, as shown in Figs. 2 and 4.

In earlier work on the study of spontaneous magnetization of ferromagnets [11], a comparison was made between direct magnetocaloric measurements and molecular mean-field simulations with the general simple exchange field, $H_{exch} = \lambda M$, where λ is assumed constant, and the use of the Brillouin function to describe field/temperature dependence of magnetization. Since the mean-field scaling method of Ref. [15] makes no such presumptions, the estimated value of the spontaneous magnetization will more closely reproduce the magnetic properties of the system. Still, the simple extrapolation of the ΔS_M vs. M^2 plots presented here produces agreeable values of the spontaneous magnetization for both a second- and a first-order magnetic phase transition systems.

The methodology presented in this work is general, and can be applied to other second- or first-order magnetic systems. Future work will consist on a more broad use of this approach, in materials such as shape-memory alloys of the Ni–Mn–Ga family, itinerant electron metamagnetic systems of the LaFeSi family, or the R–Si–Ge system (R = rare−earth).

Acknowledgments

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