A new criterion to distinguish the order of magnetic transitions by means of magnetic measurements

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A universal curve for the magnetic entropy change has been found to exist for a variety of materials with second order phase transitions. We have studied whether this universal behavior of the magnetocaloric effect is maintained in materials with first order phase transition, including $R\mathrm{Co}_2$ Laves phases and mixed $\mathrm{La}_{2/3}(\mathrm{Ca}_x\mathrm{Sr}_{1-x})_{1/3}\mathrm{MnO}_3$ manganites, which present both second order and first order magnetic ordering phase transitions. The rescaled magnetic entropy change curves for different applied fields collapse onto a single curve only for materials with second order phase transition. This universal curve may be used as a criterion for determining the order of magnetic phase transitions from purely magnetic measurements. © *2010 American Institute of Physics*. [doi:10.1063/1.3366614]

Experimental distinction between first and second order phase transitions is usually relevant to test proposed models to describe the magnetism of materials, as it has been the case for colossal magnetoresistance in manganites,[1] or the cobalt Laves phases.[2] For magnetic cooling applications, the distinction of a first order transition (FOT) from a second order transition (SOT) is relevant when designing materials that optimize the magnetic entropy change ΔS_M and refrigerant capacity (RC) near room temperature. Large values of ΔS_M and large RC are needed to build magnetic refrigerators with commercial purposes. Both quantities are usually tied to the order of the transition phase.

In one hand, large values of $|\Delta S_M|$ maximum at the transition ($\Delta S_M^{\mathrm{peak}}$), are achieved in materials with first order magnetostructural phase transitions.[3] On the other hand, high RC values depend on both the height and the width of the ΔS_M curve.[4] Although compounds with SOT show smaller $|\Delta S_M^{\mathrm{peak}}|$ than materials with FOT, the compromise between an optimal RC and the lack of hysteresis currently makes compounds with SOT better candidates for the development of magnetic cooling devices.

It is relatively common to establish the order of a transition phase by calorimetric methods. However, these experiments typically involve long measurements with small variations around T_c. Besides, conventional calorimetric measurements for nanoscopic samples are not sensitive enough to follow the rapid changes in temperature for such sample sizes.[5] Even in bulk materials that show small latent heat, such as DyCo_2, the identification of the order of the transition may not be straightforward.[6] Since in this compound the magnitude of the discontinuity in the derivative of the free energy at the transition temperature is small, their physical properties do not show steep features at the transition point. In consequence, to distinguish whether the transition has first or second order character, is not free from ambiguity.

As an alternative to calorimetric methods, the order of magnetic transitions can be established from purely magnetic measurements by employing the Banerjee criterion.[7] This technique is specially interesting for samples of nanoscopic size. Under this criterion, the presence of a negative slope region on the isotherm plots of H/M versus M^2 near the transition temperature region, indicate the first order character of the transition. However, for compounds near the critical point (such as DyCo_2), this criterion do not always work properly.[6]

A universal behavior for $\Delta S_M(T)$ curves, for different applied fields, in materials which present SOT has been recently proposed by Franco and co-workers.[8–10] The phenomenological universal curve (that can be calculated from purely magnetic measurements) consists in the collapse of entropy change curves after a scaling process, regardless the applied magnetic field. In principle, with this curve, it is possible to predict the field dependence of $\Delta S_M(T)$ even in those materials that do not follow a mean field approach. It can be used to make extrapolations in temperature or field close to the entropy change peak as well.

The existence of this universal curve for the magnetocaloric effect is based on the assumption of scaling near a second-order phase transition.[11,12] As the underlying cause for the collapse of the scaled $\Delta S_M(T)$ curves is the universal behavior from critical phenomena theory, it is natural to expect a breakdown of the universal curve for compounds with a FOT.

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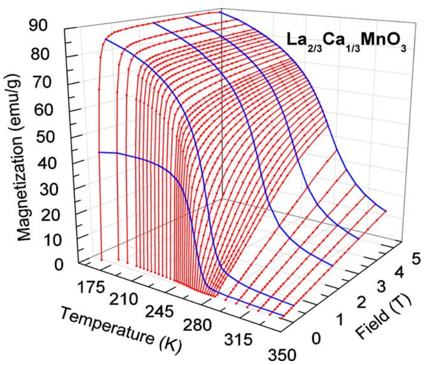

FIG. 1. (Color online) Magnetization vs field isoterms for different temperatures for $La_{2/3}Ca_{1/3}MnO_3$.

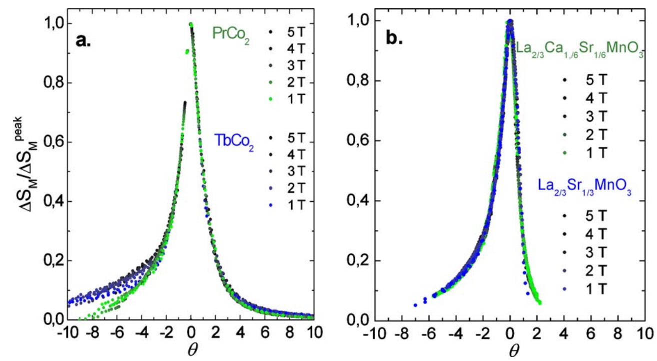

FIG. 2. (Color online) Panel a: universal behavior of the scaled entropy change curves in cobalt Laves phases compounds: $TbCo_2$ (blue dots) and $PrCo_2$ (green dots). Panel b: universal behavior of the entropy change in manganites $La_{2/3}Sr_{1/3}MnO_3$ (green dots) and $La_{2/3}(Ca_{0.5}Sr_{0.5})_{1/3}MnO_3$ (blue dots).

Within this scenario, whether or not a breakdown of the universal behavior of ΔS_M implies that the compound goes through a transition of first or second order, respectively. This assumption allows us to use this method to distinguish the order of the transition. In order to observe the validity of our statement, we have applied this method to the RCo$_2$ Laves phases which present both second order ($TbCo_2$ and $PrCo_2$) and first order magnetic ordering phase transitions ($DyCo_2$) as well as mixed $La_{2/3}(Ca,Sr)_{1/3}MnO_3$ manganites. The structural, electronic, and magnetic properties of these families of compounds have been well studied.[2,3,6,13–16]

The intermetallic RCo$_2$ samples with R=Tb, Pr, and Dy were prepared by using an induction furnace under Ar atmosphere. The alloys were later annealed under Ar atmosphere at 850 °C for 8–12 days depending on the sample. Powder samples of manganites $La_{2/3}Ca_{1/3}MnO_3$, $La_{2/3}Sr_{1/3}MnO_3$, and $La_{2/3}(Ca_{0.5}Sr_{0.5})_{1/3}MnO_3$ were obtained using La_2O_3, $CaCO_3$, Mn_2O_3, and Sr_2Co_3 as precursors. The starting powders were ground, pelleted, and sintered following a standard ceramic method. Magnetization measurements were carried out in a Quantum Design MPMS-5S superconducting quantum interference device magnetometer. $M(H)$ isotherms, for each sample, were obtained for applied magnetic fields between 0 to 5 T and the temperatures varying in a range from 6 to 400 K depending on the ordering temperature of the sample.

According to the previously reported results,[16,17] the magnetic ordering for $PrCo_2$, $DyCo_2$, and $TbCo_2$ at zero field occurs at 40, 138, and 231 K, respectively. The critical temperatures for manganites $La_{2/3}(Ca_xSr_{1-x})_{1/3}MnO_3$ have been determined to be 260, 340, and 370 K for x=1, 0.5, and 0, respectively. The manganite $La_{2/3}Ca_{1/3}MnO_3$, present a FOT, while $La_{2/3}Sr_{1/3}MnO_3$ and $La_{2/3}(Ca_{0.5}Sr_{0.5})_{1/3}MnO_3$ present a SOT.

The magnetic entropy change $\Delta S_M(T)$ can be evaluated from $M(H)$ curves, as those shown in Fig. 1, by using a numerical approximation to the equation

$$\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH, \tag{1}$$

where the partial derivative is replaced by finite differences and the integrals are solved numerically.

The construction of the phenomenological universal curve requires to normalize each isofield $\Delta S_M(T)$ to its maximum value ΔS_M^{peak} and then rescaling the temperature axis defining a new variable θ,

$$\theta = \begin{cases} -(T-T_c)/(T_{r_1}-T_c), & T \le T_c, \\ (T-T_c)/(T_{r_2}-T_c), & T > T_c, \end{cases} \tag{2}$$

The two reference temperatures T_{r1} and T_{r2} satisfy $T_{r1} < T_c < T_{r2}$. These temperatures are selected for each curve in such way that for an arbitrary value $h < 1$ such that, $\Delta S_M(T)/\Delta S_M^{\text{peak}} = h$, the reference points in the new curve correspond to $\Delta S_M(\theta = \pm 1) = h$.

Although the universal curve can be built with only one reference temperature,[12] it has been shown that the effect of the demagnetization factor[18] or the presence of a minority magnetic phase[19] can lead to a breakdown of the ΔS_M curve collapse. Two reference temperatures are used in the data treatment in order to avoid the effect of these extrinsic factors. In consequence any observed lack of the universal character in our work will not be related to them.

The normalized entropy change curves as a function of the rescaled temperature θ for compounds with magnetic SOT are shown in Fig. 2. The universal behavior for $TbCo_2$ and $PrCo_2$ can be observed in panel a, while the universal behavior for $La_{2/3}Sr_{1/3}MnO_3$ and $La_{2/3}(Ca_{0.5}Sr_{0.5})_{1/3}MnO_3$ is shown in panel b.

From these results, we can notice two interesting features. First, all normalized entropy change curves collapse onto a single curve for each compound. This result implies the validity of our data treatment for compounds with SOT in both families. Second, as it had been pointed out before, if the compounds belong to the same universality class, one can assume the magnetization curves scaling near a second-order phase transition,[11,12] i.e., the materials have the same critical exponents and in consequence their entropy change curves scale. Indeed this is observed for both ferromagnets $La_{2/3}Sr_{1/3}MnO_3$ and $La_{2/3}(Ca_{0.5}Sr_{0.5})_{1/3}MnO_3$ in Fig. 2, panel b. Correspondingly the deviation from a common universal behavior at lower theta for the $TbCo_2$ and $PrCo_2$ may be due to the fact that $TbCo_2$ is a ferrimagnet while $PrCo_2$ is a ferromagnet, therefore belonging to different universality classes. Besides, for values far from T_C the collapse does not need to hold, because in general, the scaling is satisfied close

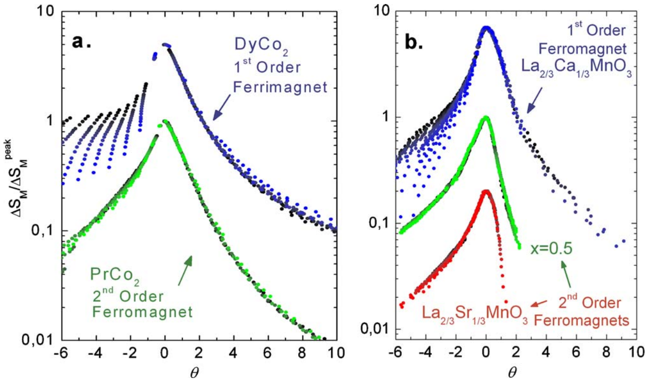

FIG. 3. (Color online) Comparison between scaled entropy change curves for materials with first and second order phase transition. In panel a RCo_2 Laves phases $DyCo_2$ and $PrCo_2$. In panel b manganites $La_{2/3}(Ca_xSr_{1-x})_{1/3}MnO_3$ with $x=0$, 0.5, 1. For the sake of clarity $DyCo_2$ and $La_{2/3}Ca_{1/3}MnO_3$ have been vertically shifted by a factor of 5 and $La_{2/3}Sr_{1/3}MnO_3$ have been vertically shifted by a factor of 1/5.

to the critical temperature (near $\theta=0$). The collapse holds disregarding the material family. This suggest that this universal behavior always takes place for compounds with SOT.

Figure 3 permits the comparison of results between compounds with FOT and SOT. Panel a shows the scaled entropy change curves for $DyCo_2$ and $PrCo_2$ in semilogarithmic axes. The difference between both behaviors is clear. Below $\theta=0$ there is no collapse for $DyCo_2$. As it was mentioned before, the first order character of the transition in $DyCo_2$ is not evident from purely magnetic measurements.[6] Nevertheless, our method allows the discrimination of the order of $DyCo_2$ transition from mere inspection of Fig. 3. The use of two reference temperatures prevents the influence of any extrinsic factor that can alter the result for in $DyCo_2$. Panel b shows the comparison between the three manganites $La_{2/3}(Ca_xSr_{1-x})_{1/3}MnO_3$ with $x=0$, 0.5, and 1. The universal behavior for SOT and its breakdown in FOT is evident also in manganites, suggesting that the breakdown of the universal behavior for the entropy change scaled curves in compounds with FOT is a general result.

In summary, the scaling of the entropy change curves leads to such different results for compounds with FOT and SOT that we can propose this construction to discriminate the order of magnetic phase transitions, as an alternative to the Banerjee criterion.

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