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Enthalpy change in the magnetocaloric effect

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We report a study of the magnetocaloric effect in magnetic systems by extracting the temperature change from the enthalpy difference between the high and the low magnetic field phases. To evaluate this alternative approach, we compare the results extracted from the proposed model with direct measurements of the adiabatic temperature change. Results obtained in the manganite compound $\text{Pr}_{0.5}\text{Sr}_{0.41}\text{Ca}_{0.09}\text{MnO}_3$ are used to show that this method is valid and useful to evaluate the magnetocaloric effect in different solid state systems, and to follow the heat dynamic of the system while a magnetic first order phase transition takes place. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4766296>]

I. INTRODUCTION

The magnetocaloric effect (MCE) is the temperature change observed in magnetic materials when an external magnetic field is applied.¹ Since the early discovery of the effect in the late 19th century,² important progress followed both in the investigation of physical aspects of the MCE and in the development of applications. The latter has become particularly important in recent years in connection to the development of more efficient and environmentally friendly solid state cooling devices. In this respect, a world wide search is in place for finding suitable magnetic materials to be used in magnetic refrigeration systems. The discovery of the giant MCE in Gd(SiGe) (Ref. 3) was an important breakpoint towards real application, substantially increasing the resulting cooling power when the material undergoes a first order magnetic transition.

The MCE in solids is produced by the entropy variation associated with the coupling of a magnetic spin system with an external magnetic field. For a magnetic system, the application of a magnetic field decreases the magnetic entropy of the system; when this process is done adiabatically, the electronic and lattice entropy contributions must increase its values to fulfill the adiabatic condition. When the electronic contribution can be neglected, an increase in the lattice thermal entropy yields a temperature increase of the magnetic material. In some cases, the application of a magnetic field increases the entropy, giving rise to the inverse magnetocaloric effect (IMCE).^{4,5} A contribution to the understanding of both MCE and IMCE in ferromagnetic (FM) and antiferromagnetic systems was performed by von Ranke *et al.*⁶

The methods used to study experimentally the MCE can be divided in two general categories: direct and indirect measurements. In the direct methods, the temperature change is measured by recording the sample temperature during the application of the magnetic field. In the indirect methods, magnetization and specific heat measurements are used to estimate the change in temperature. Because the direct methods present more experimental difficulties,^{7,8} the indirect

methods are most commonly used to study the MCE. The entropy change is derived from magnetization measurements using a Maxwell relation, allowing the calculation of ΔS by numerical integration of a set of magnetization curves. This method can be successfully used in many cases,⁹ but care must be taken when first-order transitions are present, or in systems with slow dynamics or frozen states.^{10–12} In those cases, the entropy change can be directly associated with the enthalpy change during the transition and a major effort must be made to take in to account this entropy variation.^{13,14} The discrepancy between the measured adiabatic temperature change during a first order transition and that predicted using Maxwell's relation has been pointed out in several works,^{10,15} and was attributed to the kinetics of the first order transition.¹⁵

In this work, we present a study on the temperature change experimented by a typical manganite compound, $\text{Pr}_{0.5}\text{Sr}_{0.41}\text{Ca}_{0.09}\text{MnO}_3$, during the first order transition between the high temperature ferromagnetic phase and the low temperature charge ordered antiferromagnetic state, occurring at temperatures around 160 K. We record the temperature change as a function of time while the applied magnetic field is raised. A dynamic model for the magnetocaloric effect is used to describe the time evolution of the system temperature, based on an alternative approach to the calculation of the MCE considering the enthalpy change during the transition instead of the entropy, similar to that employed previously.¹⁶ The close agreement observed between experimental and calculated data gives confidence on the approach employed.

II. EXPERIMENTAL DETAILS

Polycrystalline samples of $\text{Pr}_{0.5}\text{Sr}_{0.41}\text{Ca}_{0.09}\text{MnO}_3$ were obtained by the standard techniques.¹⁷ Magnetization and specific heat were measured using a commercial Quantum Design Physical Properties Measurement System (PPMS). The temperature change was measured directly using a home made system in a Janis 7 T cryostat, using an alumina sample

holder with a Cernox temperature sensor. The system was placed in a superconducting magnet in a chamber with high vacuum to favor the thermal insulation.

III. THEORETICAL CONSIDERATIONS

We start considering the case of a magnetic first order transition induced by the application of an external magnetic field. In terms of the enthalpy E of the system, the released heat can be expressed as

$$dQ = \left[\left(\frac{\partial E}{\partial p} \right)_{T,H} - V \right] dp + \left[\left(\frac{\partial E}{\partial H} \right)_{T,p} + M \right] dH + \left(\frac{\partial E}{\partial T} \right)_{p,H} dT. \quad (1)$$

In a real first order transition from a non-ferromagnetic (NF) phase to a FM one, in which both phases coexist in a range of field and temperature, the enthalpy of the system as a function of the applied magnetic field H changes due to two factors: the change of the relative amount of the coexisting phases and the change of the magnetization of the FM fraction. Taking E_{FM} (E_{NF}) as the enthalpy of the FM (NF) phase, and x the fraction of the FM phase in the coexisting region, the total enthalpy can be written as

$$E = xE_{FM} + (1-x)E_{NF} \quad (2)$$

Assuming that the application of a magnetic field only affects the enthalpy of the FM phase, that is, $E_{NF} \neq E_{NF}(H)$ and $E_{FM}(H) = E_{FM}(0) - M_S H$ (where M_S is the T and H dependent magnetization of the homogeneous FM phase), we obtain for Eq. (1) in the isobaric case

$$dQ = \left[\frac{\partial x}{\partial H} (E_0 - M_S H) - xH \frac{\partial M_S}{\partial H} \right] dH + C dT, \quad (3)$$

where $C = \left(\frac{\partial E}{\partial T} \right)_{p,H}$ is the heat capacity of the system at constant pressure and magnetic field.

In adiabatic conditions, the exchanged heat is zero, and Eq. (3) allows us to obtain the adiabatic temperature change of the system. In non adiabatic conditions, when the coupling between the system and the environment cannot be neglected, Eq. (3) gives the possibility to study the heat dynamic of the whole system. Hereafter, we will show how the analysis based on enthalpy change successfully describes the MCE in systems which display magnetic first order phase transitions.

IV. RESULTS

We will now show how the analysis of the MCE in terms of enthalpy can be applied to the manganite compound $\text{Pr}_{0.5}\text{Sr}_{0.41}\text{Ca}_{0.09}\text{MnO}_3$, which presents simultaneous and correlated structural and magnetic phase transitions.¹⁸ These transitions can be readily observed in the temperature dependence of the magnetization, presented in Fig. 1(a). On cooling, a first transition, around $T_c = 250$ K corresponds to the appearing of the ferromagnetic metallic phase. This is also evidenced in the

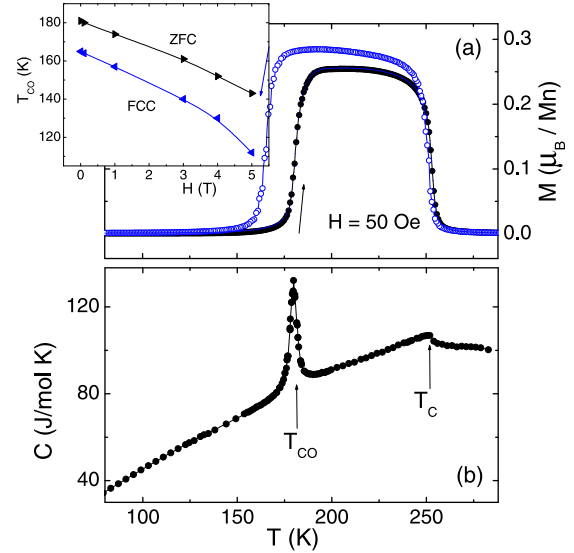


FIG. 1. Temperature dependence of the magnetization (a) and specific heat of $\text{Pr}_{0.5}\text{Sr}_{0.41}\text{Ca}_{0.09}\text{MnO}_3$. The inset shows the charge order transition temperature, $T_{CO}(H)$ for various applied fields, measured with ZFC and FCC procedures.

change of slope in specific heat C , shown in Fig. 1(b). At this temperature, a structural transition was observed by neutron diffraction,¹⁹ from spatial group Imma to I4/mcm . The second transition, at $T_{CO} = 180$ K corresponds to the charge ordering antiferromagnetic transition (CO-AF), producing a well defined peak in C at the same temperature. The transition is also structural,¹⁹ from spatial group I4/mcm to Pmmm . The transition at T_{CO} is hysteretic, whereas the FM transition is not. The inset of Fig. 1 shows how T_{CO} changes with H , both in the field cooled cooling (FCC) and zero field cooled (ZFC) measurements. A decrease in the transition temperature as the field increases is observed.

At temperatures below T_{CO} , magnetization measurements as a function of applied field, $M(H)$, present a metamagnetic transition, as shown in the main panel of Fig. 2.

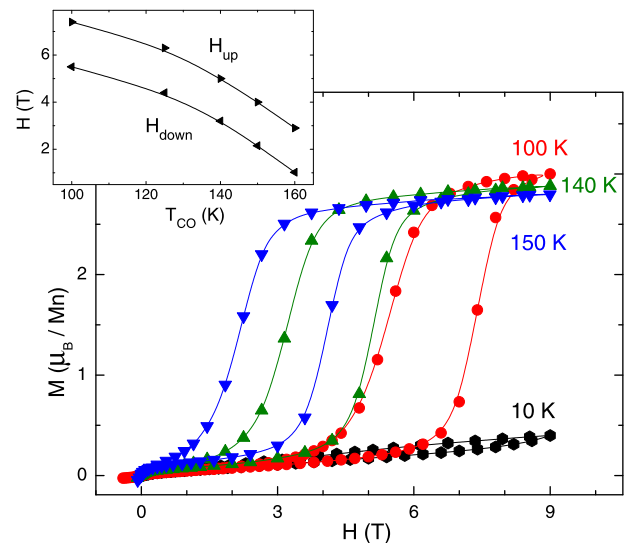


FIG. 2. Magnetization plotted as a function of field, $M(H)$ for various temperatures. The inset shows the metamagnetic field, extracted on the increasing and decreasing field branches.

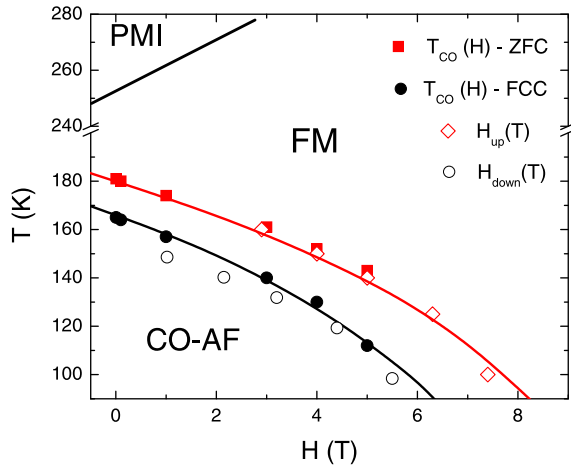


FIG. 3. Magnetic phase diagram $\text{Pr}_{0.5}\text{Sr}_{0.41}\text{Ca}_{0.09}\text{MnO}_3$.

The saturation magnetic moment is close to the expected theoretical value when considering the entire sample as FM with noninteracting magnetic moments. The metamagnetic transition is also hysteretic with field. At temperatures below 100 K, it is not possible to reach the saturation magnetic moment with the highest available magnetic field, $H = 9$ T. With the data extracted from magnetization measurements, it is possible to obtain, through simple considerations, the H and T dependence of x and M_s . The phase diagram of the system can be also extracted from magnetization measurements, as displayed in Fig. 3. The points extracted from $M(H)$

curves match with those extracted from $M(T)$ measurements, indicating that the final state does not depend on the path taken in the H - T plane.

Following the Clausius-Clayperon relations, it is possible to extract from the data of Fig. 3 the values for $E_0 = (300 \pm 10)$ J/mol and for the difference between the entropies of the phases involved at zero field, $\Delta S = 1.82$ J/mol K. A similar value for ΔS is obtained by integration of the peak in the C/T - T graph.

In order to study the temperature change during the metamagnetic transition, we have measured the sample temperature as function of time while the magnetic field was increased at a fixed rate, starting at temperature of 150 K, as plotted in Fig. 4(a). Figure 4(b) shows the same measurements but displayed as a function of H . With increasing field, no change in temperature is observed for H below 3 T ($t = 1250$ s.). Between 3 T and 5 T, when the metamagnetic transition takes place, a major change is observed in the sample temperature. During this transition, the temperature decreases by approximately 0.5 K, followed by an exponential relaxation to the base temperature. The characteristic relaxation time, $\tau \approx 400$ s, is a measurement of the thermal link between the sample and the external chamber. In the downward cycle, we see the opposite behavior, an increase of the sample temperature in the region where the AFM-FM transition takes place. After that, the system relaxes to the bath temperature with the same characteristic time than that observed in the upward run. The same behavior was observed in subsequent cycles.

The heat dynamic involved in the process can be described using Eq. (3) and considering the exchange between the sample and the environment, with characteristic coupling time τ . The equation for the heat flux exchange is then

$$\frac{(T - T_0)}{\tau} = -\frac{1}{C + C_{SH}} \left[\left(\frac{\partial E}{\partial H} \right)_{T,p} + M \right] \frac{dH}{dt} - \frac{dT}{dt}, \quad (4)$$

where C and C_{SH} are the sample and the sample holder heat capacity, respectively, in the assumption that the characteristic thermal coupling time between sample, sample holder, and thermometer is $\tau_{\text{int}} \ll \tau$. Finally, replacing the magnetic field dependence for the enthalpy, Eq. (4) becomes

$$\frac{(T - T_0)}{\tau} = -\frac{1}{C + C_{SH}} \left[\frac{\partial x}{\partial H} (E_0 - M_S H) - x H \frac{\partial M_S}{\partial H} \right] \frac{dH}{dt} - \frac{dT}{dt}. \quad (5)$$

This equation can be easily integrated to obtain the time evolution of the sample temperature. All the parameters and functions involved were determined through independent magnetization measurements. In Fig. 4, we display the calculated evolution of the sample temperature as a function of time, compared with the measured one at a base temperature of 150 K, showing the close agreement between the experimental and the calculated data in the whole magnetic field cycle.

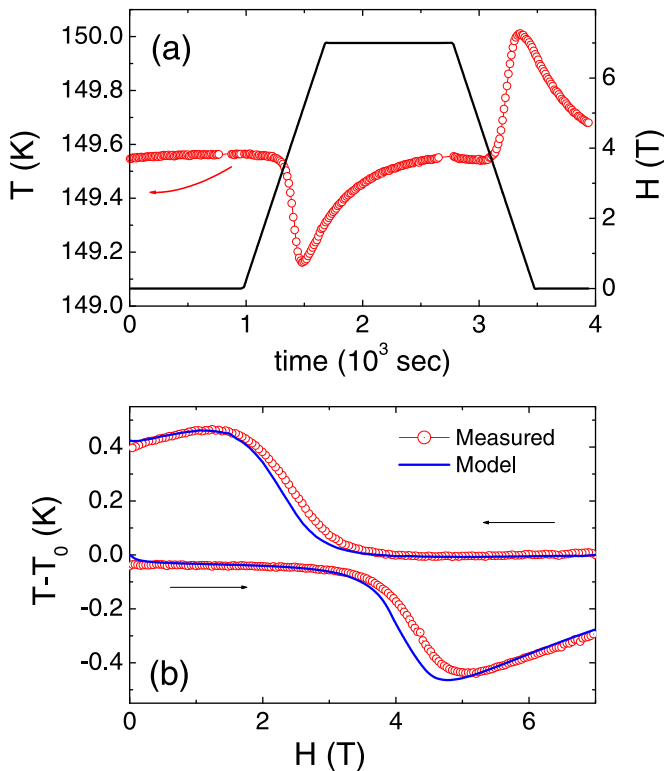


FIG. 4. (a) Time evolution of sample temperature (red symbols) during the application of an external magnetic field (black line); (b) magnetic field evolution of the measured (red symbols) and predicted (blue line) sample temperature. The prediction was made by numerical integration of Eq. (5) (see text for details).

V. CONCLUSIONS

In this work, we presented and discussed an alternative approach to analyze the magnetocaloric effect in terms of the enthalpy change. This approach is an alternative possibility to account the MCE from indirect measurements. From a thermodynamic point of view, the enthalpy approach is equivalent to the most commonly used method where the entropy change is extracted from magnetization measurements through a Maxwell relation. However, our method can be used in cases where the magnetization does not provide an adequate description of the thermodynamic state of the systems due to the presence of a first order transition. In these cases, the approach based on enthalpy evaluation successfully describes the sample temperature change during the transition. This is one of the key parameters to be measured when the magnetocaloric effect is being studied using direct methods, and configures the most important feature for technological applications. As an example, we applied the model to a manganite compound in almost adiabatic conditions, reaching a good agreement between the model and the measured data. This approach can give some insight in the description of magnetocaloric effect in magnetic first order transitions involving non equilibrium states, arrested kinetics or frozen dynamic.

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