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TOWARDS A CONSISTENT THERMODYNAMIC MODEL OF MAGNETOCALORIC MATERIAL FROM EXPERIMENTAL CHARACTERIZATION

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ABSTRACT—Magnetocaloric material (MCM) measurements and data treatments are essential for modeling and developing magnetic refrigeration system. The paper discusses the thermodynamic relevance of the material model considered and proposes a suitable strategy. Models consistent with thermodynamics are essential for computation of coefficient of performance (COP) of refrigeration system. The study is supported by the knowledge of intrinsic material characteristics and analyses of thermodynamic behaviors. It is applied on a second order phase transition material $Pr_{0.65} Sr_{0.35} MnO_3$.

1. INTRODUCTION

MCM practical characterization leads to magnetization, heat capacity [1] and adiabatic temperature change as a function of temperature and applied field. These raw data are subjected to several measurement errors. In addition, they should be processed and analyzed to be properly used. Firstly, the data are connected to the internal field to have intrinsic properties $M(H, T)$, $c_H(H, T)$, $\Delta T_{adia}(H, T)$, using demagnetizing factor N and the relation $H = H_{applied} - NM$. This method is relevant when applied on a long parallelepiped specimen providing a homogeneous field distribution in a sample. This condition is fulfilled in a magnetometer but not in a calorimeter in which the field is generally applied along the transverse direction to enhance heat transfer. Afterwards these data are fitted and interpolated to provide mathematical models with the risk of introducing user information not in accordance with thermodynamics. All of this breaks the deep data connection through thermodynamics laws, which can be expressed with the closed differential forms of the state function. In this paper, we define the thermodynamic consistency which guarantees the energy conservation. Then, we analyze it and point out the problem in the case of the interpolated and fitted data of a $Pr_{0.65} Sr_{0.35} MnO_3$ sample. Finally, we propose a solution which merges data and thermodynamics with least square method (LSQ) to build an estimated entropy from which M , c_H , ΔT_{adia} can be derived.

2. THERMODYNAMICS

The system considered is an elementary volume of MCM which is sufficiently small to be considered infinitely near an equilibrium state. The thermodynamics laws give the following relations in which u , s and s_{irr} correspond to the internal energy, entropy and irreversible entropy per unit of volume. B is the magnetic flux density. For reversible material and adiabatic conditions, Eq. (1) and (2), through magnetization and demagnetization leads to the same temperature and does not introduce hysteresis in the magnetization curve. Based on this analysis, the tested MCM is considered reversible and the term s_{irr} is null.

$$du = Tds - T\delta s_{irr} - MdB \quad (1)$$

$$Tds = \delta Q + T\delta s_{irr} \quad (2)$$

$$\int_{cycle} Tds = \int_{cycle} MdB \quad (3)$$

du being a closed differential form of degree 1, T and M are the partial derivatives of u with respect to s and B and the cross derivatives are equal. This condition could be seen as energy conservation on an elementary cycle and leads to Eq. (3). For a second order transition material, when H and T are taken as state variables, the Maxwell relation $\frac{\partial s}{\partial H} = \mu_0 \frac{\partial M}{\partial T}$ is deduced from Eq. (1). It expresses the transfer between the thermal and magnetic energy, when the terms $\frac{\partial s}{\partial T}$ and $\frac{\partial M}{\partial H}$ is linked to exchange conservative energy in respectively thermal and magnetic form. The main issue is that entropy is not directly accessible. Only $T \partial s / \partial T$ and M are measurable. Moreover calorimetric measurements are less accurate than magnetometry but M data has to be differentiated. In practice, we get derivative of s with uncertainties noted as ϵ_1 and ϵ_2 , e.g. if adiabatic thermodynamic cycle is numerically simulated, uncertainties behave as source term producing or absorbing heat and magnetic work (4). And because the COP is badly conditioned, uncertainties hardly affect the COP evaluated from heat exchange.

$$\int_{cycle} Tds = \int_{cycle} \left(T \frac{\partial s}{\partial T} + \epsilon_1 \right) dT + \left(T \frac{\partial s}{\partial H} + \epsilon_2 \right) dH \quad (4)$$

Thermal capacity and $\partial M / \partial T$ has to be derivable from the same and unknown entropy function and to be in accordance with measurements. All the information is merged using weighted least squares (LSQ) method. LSQ consists in minimizing $(AS - B)^T W (AS - B)$ where S is the column matrix of entropy grid values and W is the weighted matrix. Each line of system $(AS = B)$ represents a constraint. To solve LSQ, several numerical algorithms are developed and compared.

The choice of weighted matrix depends on the accuracy of measurements and their number. Indeed, magnetometer and calorimeter data is balanced. As calorimeter data are less numerous than those of the magnetometer, their weights are increased. In addition, we assume that transition is better caught near zero field with the magnetometer and increase the data weights in this range.

3. MEASUREMENT, RESULT AND DISCUSSION

The study is conducted on a second order phase transition material $\text{Pr}_{0.65}\text{Sr}_{0.35}\text{MnO}_3$. Measurements are performed on both magnetometer and calorimeter with respectively demagnetizing factor of 0.45 and 0.06. The 2D interpolation is done with smooth spline of degree two. Fig. 1 shows all the data and their analysis.

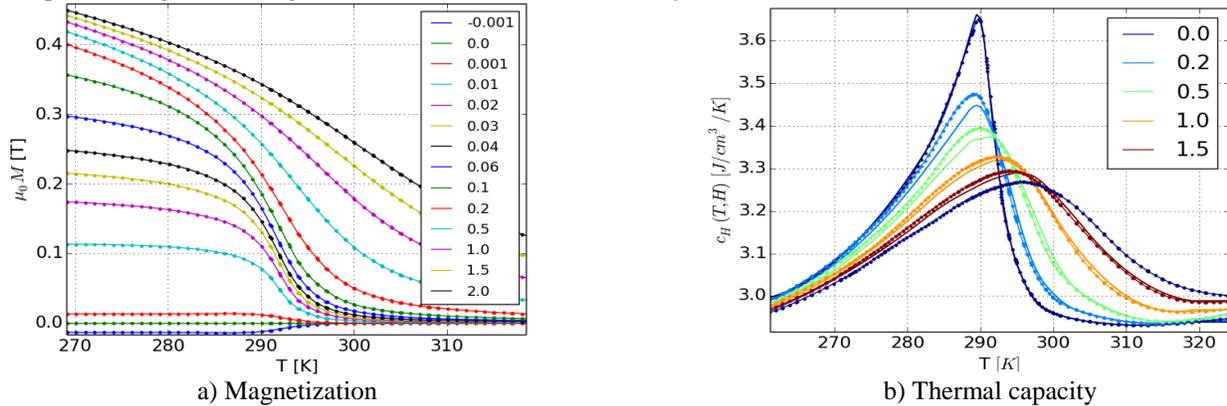


Fig.1. Magnetization and thermal capacity as a function of temperature and magnetic field
 Dots: raw measured data vs applied field $\mu_0 H_{\text{applied}}$, lines: interpolated data function vs internal field $\mu_0 H$.

The LSQ method is applied to correct the c_H to be in accordance with magnetization to thermodynamics (Fig. 2). Then numerical simulations of Brayton Cycle [2] and computation of COP using two theoretically equivalent methods are done. The results given in Fig. 3 highlight that the magnetic method ($Q_{\text{cold}}/W_{\text{mag}}$) is much more robust than the thermal one ($-Q_{\text{cold}}/(Q_{\text{cold}} + Q_{\text{hot}})$). The LSQ method allows the discrepancy on COP computed with thermal method to be strongly reduced: from the range of 1000 to -200 with interpolated data to a rational range of 250 to 280 with LSQ data.

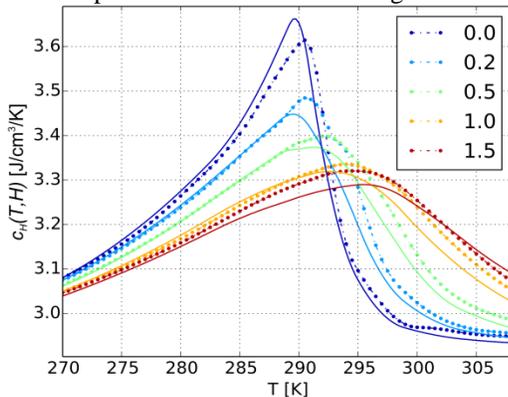


Fig. 2. Thermal capacity vs T and $\mu_0 H$
 Dots: LSQ data, line: 2D interpolated data

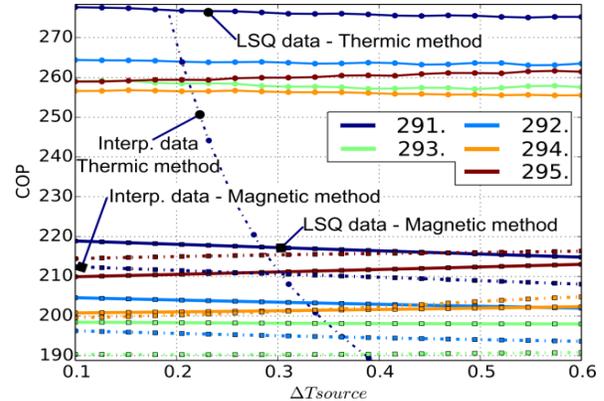


Fig. 3. COP: dash: interpolated data, line: LSQ data
 • thermic method " TdS ", ■ magnetic method " MdB "

This study shows that the thermodynamic consistency is weak through experiment, interpolation, and numerical method for the cycle computation. To face this, accurate models of materials characteristics are required. In this paper we highlight that the magnetic method is more robust and propose the LSQ method to improve the COP estimation via the thermal method.

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