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Properties of magnetocaloric materials with a distribution of Curie temperatures

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ABSTRACT

The magnetocaloric properties of inhomogeneous ferromagnets that contain distributions of Curie temperatures are considered as a function of the width of such a distribution. Assuming a normal distribution of the Curie temperature, the average adiabatic temperature change, ΔT_{ad}, the isothermal magnetic entropy change, Δs, and the heat capacity, c_p, in zero magnetic field and an applied magnetic field of $\mu_0 H = 1$ T, have been calculated using the mean field model of ferromagnetism. Interestingly, both the peak position and amplitude of each of these parameters vary differently with the width of the distribution, explaining the observed mismatch of peak temperatures reported in experiments. Also, the field dependence of ΔT_{ad} and Δs is found to depend on the width of the distribution.

1. Introduction

Magnetic refrigeration relies on the heating and cooling of a magnetocaloric material due to the application and removal of a magnetic field, see, e.g., Ref. [1]. This so-called magnetocaloric effect has a maximum value close to, but not generally coinciding with, the magnetic phase transition temperature of the magnetocaloric material. Hence, for applications where high values of the magnetocaloric effect are desired, it is important to know the transition temperature (Curie temperature) with some degree of accuracy. In some magnetocaloric materials the Curie temperature may be controlled by, e.g., chemical doping. Here materials may be tailored to specific applications.

In order to achieve high temperature spans in magnetic refrigeration devices layered regenerators consisting of a number of different magnetocaloric materials may be used. Such graded regenerators are often built from a number of similar materials with a relatively small spacing of the transition temperatures [2,3]. Examples of such materials that may be chemically doped in order to tune the Curie temperature include $La(Fe,Co,Si)_{13}$ [4], $La_{0.67}Ca_{0.33-x}Sr_xMnO_3$ [5] and $Gd_{1-x}Tb_x$ or $Gd_{1-x}Er_x$ [2]. The required spacing between the transition temperatures will depend on the application, but will in general be of the order of the adiabatic temperature change, i.e. a few degrees. To achieve a tuning of the Curie temperature on such a small scale requires an accurate control of the composition and of any spatial inhomogeneities. Thus a consistent method for analyzing and reporting the temperature dependence of the magnetocaloric effect in these materials is needed.

In general three physical properties are needed to characterize the magnetocaloric effect fully [6]. The first is the isothermal magnetic entropy change, Δs, linked to the magnetization, m, in a magnetic field change from H_1 to H_2 through

$$\Delta s = -\mu_0 \int_{H_1}^{H_2} \frac{\partial m}{\partial T}\, dH, \tag{1}$$

where μ_0 is the vacuum permeability and T is the temperature. The other two properties are the specific heat capacity, $c_p(T,H)$, and the adiabatic temperature change, ΔT_{ad}, given by

$$\Delta T_{ad} = -\mu_0 \int_{H_1}^{H_2} \frac{T}{c_p}\frac{\partial m}{\partial T}\, dH. \tag{2}$$

At the lowest fields the derivative $\partial m/\partial T$ is large very close to the Curie temperature in materials displaying a second order phase transition. As the field is increased the inflection point of m will gradually move to higher temperatures, while $\partial m/\partial T$ rapidly decreases. Thus, if the initial field H_1 is close to zero and H_2 is a modest field up to about 1 T both integrals in Eqs. (1) and (2) will give rise to peaks that will be almost coincident with the Curie temperature, as found in, e.g, Refs. [7,8].

Using readily available analysis lab equipment, c_p, at least in zero applied field, can be fairly easily measured, whereas calculating Δs from Eq. (1) requires an extensive set of magnetization data if high accuracy is required. ΔT_{ad} may be calculated from Eq. (2), requiring the aforementioned magnetization data as well as knowledge of the field dependence of c_p. Alternatively it may be directly measured, but this requires non-standard, often custom built lab equipment [8]. Finally, Δs and ΔT_{ad} may be

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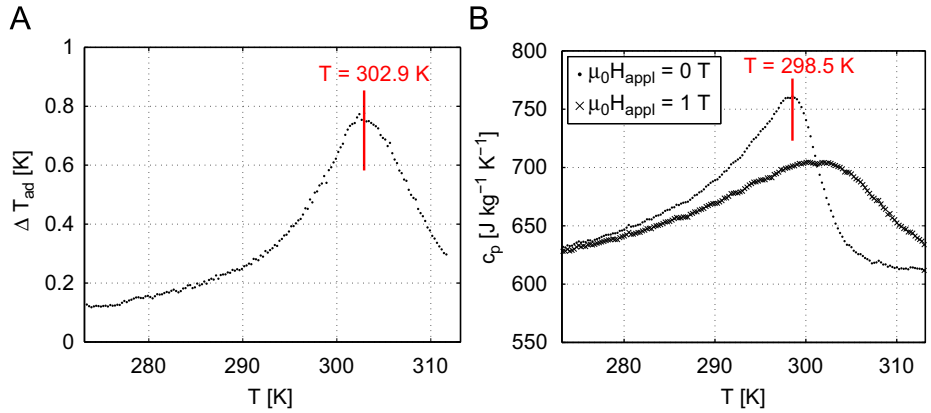

Fig. 1. Experimentally measured values of (A) ΔT_{ad} in an applied field of $\mu_0 H = 1$ T and (B) c_p in zero and 1 T applied field for a sample of $La_{0.66}Ca_{0.24}Sr_{0.09}Mn_{1.05}O_3$. The vertical lines indicate the peak temperatures. A difference in the peak temperature of 4.4 K is observed. The data is corrected for demagnetisation.

derived from heat capacity data using the functional relationship $s(T,H_1) = s(T+\Delta T_{ad},H_2)$ and $s(T,H_1) = s(T,H_2)+\Delta s(T,H_1 \rightarrow H_2)$, valid for materials with a second order phase transition.

For the reasons outlined above the magnetocaloric parameters most often reported in the literature are zero field c_p and Δs, and the peak temperature of either of these is often referred to as the Curie temperature of the material.

Differences between the peak temperatures found in the three parameters when measuring the same sample have been observed for, e.g., $La_{0.66}Ca_{0.24}Sr_{0.09}Mn_{1.05}O_3$ measured at Risø DTU using the equipment discussed in Ref. [8]. Here the zero field c_p peaks at about 4.4 K below the value where ΔT_{ad} peaks, as shown in Fig. 1.

Similar discrepancies have been observed in other manganite systems, where the peak temperature of c_p has been found to be less than the Curie temperature determined as the inflection point of m in an applied field of 10 mT [9], the peak of Δs [9–11] and the metal-insulator transition [12]. Reductions of the peak temperatures of c_p have also been observed in other classes of magnetocaloric materials, e.g. $Tb_5Si_2Ge_2$ [13] and $La(Fe,Co,Si)_{13}$ [14].

A local distribution in Curie temperatures within a material may arise due to differences of the exchange environments of the magnetic ions because of, e.g., defects, strain or impurities in the structure. In the following we will show how such a distribution of Curie temperatures within a material will influence measurements of each of the magnetocaloric properties. It has previously been shown, by numerical modeling, how a normal distribution of Curie temperatures can shift the peak of Δs to lower temperatures [15]. Here, we confirm this result and expand the study to include the influence on c_p and ΔT_{ad} of the width of the distribution. The distribution is introduced through the mean field model of ferromagnetism to calculate the temperature and field dependence of the magnetization (see, e.g., Ref. [16]) as this is a robust model known to give correct trends for a large number of materials. This model is combined with the Debye and Sommerfeld models to include the full heat capacity in the calculations [17]. In the following this combined model will simply be referred to as MFM.

2. Numerical simulation results

The MFM results have been calculated using the parameters of gadolinium as given in Ref. [18]. Gadolinium was chosen as the model system due to its role as benchmark material for magnetic refrigeration and a fairly good agreement between MFM results and experimental data, see, e.g., Ref. [19]. The entropy change and adiabatic temperature change are calculated from the magnetization and heat capacity using Eqs. (1) and (2).

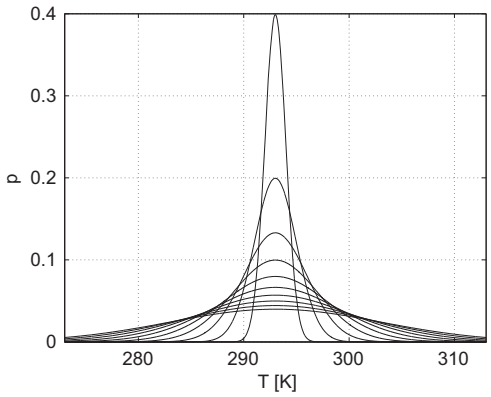

Fig. 2. The distributions of Curie temperatures used in the present study. The range of standard deviations shown is $\sigma = 1$ K–10 K and p is the probability.

In a sample having a distribution of Curie temperatures, the measured values of Δs, c_p and ΔT_{ad} will be spatial thermal averages over the entire sample. The basic premise of the present study is that the spatial average may be replaced by an average over an ensemble of spatially uniform samples having a randomly distributed Curie temperature. This will be the case if the variation of the Curie temperature occurs on a scale which is much less than the size of the sample. Then each small part of the sample only feels the average magnetic properties of the rest of the sample, since the internal field in the sample only varies on the same scale as the sample itself.

In the opposite case, when the spatial variation of the Curie temperature occurs on a scale comparable to the sample size (as in the case, e.g., of a graded material), it is essential to include demagnetization effects [20].

Normal distributions of 10,000 random Curie temperatures have been used as input for the MFM to simulate having a distribution of Curie temperatures. All other input parameters have been kept constant in these calculations. Each of the normal distributions of Curie temperatures is centered around 293 K and characterized by its standard deviation, σ. Values in the range $\sigma = 0$ K–10 K are modeled in order to simulate different degrees of impurities or defects. The distributions used in this study are shown in Fig. 2.

Using MFM with the distributions of Curie temperatures outlined above, the final values of the magnetocaloric parameters when the sample is in thermal equilibrium have been calculated. For the values of the specific entropy and heat capacity this simply corresponds to an average of the values for the random Curie