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A Preisach approach to modeling partial phase transitions in the first order magnetocaloric material MnFe(P,As)

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ABSTRACT

Magnetic refrigeration is an emerging technology that could provide energy efficient and environmentally friendly cooling. Magnetocaloric materials in which a structural phase transition is found concurrently with the magnetic phase transition are often termed first order magnetocaloric materials. Such materials are potential candidates for application in magnetic refrigeration devices. However, the first order materials often have adverse properties such as hysteresis, making actual performance troublesome to quantify, a subject not thoroughly studied within this field.

Here we investigate the behavior of MnFe(P,As) under partial phase transitions, which is similar to what materials experience in actual magnetic refrigeration devices. Partial phase transition curves, in the absence of a magnetic field, are measured using calorimetry and the experimental results are compared to simulations of a Preisach-type model. We show that this approach is applicable and discuss what experimental data is required to obtain a satisfactory material model.

1. Introduction

With the global focus on energy and new developments in room temperature magnetocaloric materials (MCM), the field of magnetic refrigeration has grown a lot within the last 15 years. Magnetic refrigeration utilizes the magnetocaloric effect (MCE), where a temperature change in the MCM is induced when a magnetic field is applied. Under adiabatic conditions, the total entropy remains constant and the decrease of magnetic entropy is balanced by an increase in lattice entropy and thus a temperature increase. The effect is completely reversible in the case of second order materials and a cooling effect is obtained upon removing the magnetic field.

The temperature increase is largest around the Curie temperature, T_C, but it is only of the order of a couple of degrees for an applied magnetic field of one tesla. In order to be useful in applications it must therefore be amplified through using Active Magnetic Regenerators (AMR), where the MCM undergoes thermodynamic cycles through magnetization, demagnetization and heat exchange with a fluid in order to cool a system. For a general review of magnetic refrigeration, see Smith et al. [1].

Many promising new materials are being researched, and some of these are the first order materials that have a coupled magnetic and structural phase transition, leading to a large entropy change during a transition. However, these materials have some degree of thermal and magnetic hysteresis, which is problematic in several ways. Hysteresis leads to heat production in the material during each cycle, which reduces the cooling capacity of the system. More importantly, the state variables, the magnetization M and the entropy s, become history dependent, making realistic predictions of performance and use of simple datasets in AMR modeling non-trivial. The characterization of the MCE is often done by mapping the complete phase transition through saturation loops. However, in an AMR cycle the MCM will rarely undergo a complete phase transition, but only cycle through minor loops. The trace of these minor loops depends on the specific, material dependent, properties of the phase transition and will influence the AMR performance.

Here we investigate the hysteresis properties of the partial first order phase transitions of the magnetocaloric material MnFe(P,As). The class of compounds MnFe(P,X), with X=As,Ge,Si is of high interest for application to magnetocaloric refrigeration because the phase transition temperature and hysteresis can be carefully tuned by changing the stoichiometry [2] and the raw materials are inexpensive compared to other MCMs.

For this study, a material composition with a small degree of hysteresis is chosen. The partial phase transitions are characterized by a differential scanning calorimeter (DSC) where the heat

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flux, q, needed to change the sample temperature at a given rate is measured. From this the entropy, s, is deduced and used as the material state variable. The experimental results are analyzed and compared to a Preisach-type thermodynamic model of the phase transition, suitable for out-of equilibrium phenomena [3].

2. A Preisach model approach

The modeling approach employed here is based on the idea of decomposing the hysteretic behavior of the system in terms of a superposition of a collection of bistable units.The output of each unit is the phase state, $x=\{0,1\}$, in our magnetic case corresponding to the paramagnetic (PM) and ferromagnetic (FM) phase states for the magnetocaloric material, respectively (Fig. 1). Each unit is characterized by two parameters (g_u, g_c), which give the unit specific switching fields $Z_\beta=g_u+g_c$ and $Z_\alpha=g_u-g_c$ that determine when the unit is forced to be in either phase 0, $Z\le Z_\alpha$, or phase 1, $Z\ge Z_\beta$. The hysteretic behavior appears in the intermediate field region $Z_\alpha<Z<Z_\beta$, where the unit remains in its current phase. The energy landscape for an individual unit is shown in Fig. 1, from which the meaning of (g_u, g_c) can be visualized.

The model input field, Z, that drives the unit transitions depends on the intensive variables, i.e. the magnetic field H and temperature T. Z is assumed the same for all units and is given by the difference in the Gibbs free energy of phase 0 and 1

$$Z(H,T)=\frac{g_0(H,T)-g_1(H,T)}{2}. \tag{1}$$

The functions $g_0(H,T)$ and $g_1(H,T)$ are the equilibrium Gibbs free energies of the two pure phases, far away from the transition. These are assumed single-valued functions of both H and T.

The total model output is determined by the collection of bistable units lying in the (g_u, g_c)-plane, the Preisach plane. The distribution of these units is given by the Preisach distribution $p(g_u, g_c)$. The Z-field then dictates which areas of the plane that are switched or maintained in their current phase and the time evolution of $Z(t)$ create the history dependent transition line $b(g_c)$, as illustrated in Fig. 2.

The current FM phase fraction is determined by integration in the Preisach plane

$$X=\int_0^{+\infty} dg_c \int_{-\infty}^{b(g_c)} p(g_u,g_c)dg_u. \tag{2}$$

The entropy of the mixed phase state is then given as

$$s=(1-X)s_0+Xs_1 \tag{3}$$

where s_0 and s_1 are the PM and FM pure phase entropies, respectively.

To model the phase transformation one has to know the pure phase Gibbs free energies, g_0 and g_1, and the Preisach distribution $p(g_u, g_c)$, which can be inferred from experiments, as shown in the following section.

In this paper this approach is tested by comparing the model to the measured hysteresis in s vs. T of MnFe(P,As) at the first order magnetoelastic phase transition.

3. Calorimetric measurements

For this study the first order material MnFe(P,As), provided by BASF Gmbh, has been used. It has a hexagonal Fe_2P structure and a magnetic phase transition between the low temperature FM state and the high temperature PM state [4]. The phase transition is magnetoelastic, coupling the magnetic transition with a structural transition. Around the transition temperature the lattice parameter ratio, c/a, of the hexagonal unit cell changes, while the volume remains approximately constant [2].

A 35 mg sample, measuring $2\times2\times1\ \mathrm{mm}^3$, with $T_C\approx297$ K was measured with a power compensation DSC. Each measurement was initiated with the sample being in the FM state by cooling it to 273 K. The measured data is the heat flux q absorbed by the sample in order to maintain a constant temperature-scanning rate of $\dot{T}=\pm2\ \mathrm{K\,min^{-1}}$, which corresponds to a scaled heat capacity

$$c=\frac{q}{\dot{T}}. \tag{4}$$

An example of the measured data is shown in Fig. 3. The results have been corrected for thermal lag, due to the heat transfer time between the sample and the sample chamber. Assuming a constant thermal contact resistance R between the sample and the chamber where the temperature is measured, this correction leads to a shift between the sample temperature T and the measured temperature T_m, $T=T_m-R\,q$. The resistance is determined by measuring q at different temperature rates and is estimated to $R=160\ \mathrm{K\,W^{-1}}$.

3.1. Modeling the material properties

Obtaining expressions for the pure phase properties of the material is done from the heat flux measured away from the phase transition. Fig. 3 shows data from the directly measured heat flux, where a thermal hysteresis of about 1.5 K is seen.

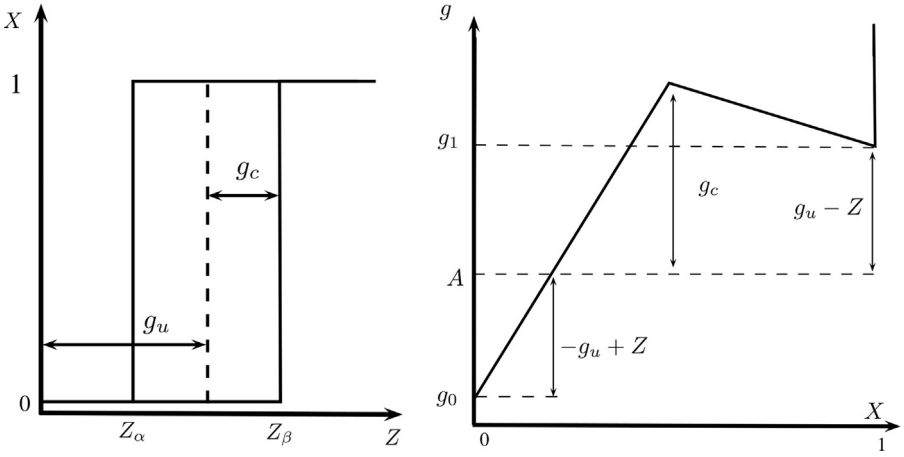

Fig. 1. (Left) A bistable hysteretic unit, defined by the parameters (g_u, g_c). (Right) The energy landscape of a unit in the presence of the Z-field.