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Theoretical investigation on the magnetocaloric effect in MnAs using a microscopic model to describe the magnetic and thermal hysteresis

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ABSTRACT

We report the thermal and magnetic hysteresis diagram for MnAs that comes from a microscopic description of a magnetic system through a model Hamiltonian that takes into account the magnetoelastic interaction. The temperature and magnetic hysteresis intervals are governed by the magnetoelastic interaction parameter, which leads to the energy barrier between stable and metastable minima in the exact free energy, obtained from our microscopic model. Application of the model to the MnAs first-order magnetic material, which presents high hysteresis effect, leads to a good agreement with the experimental magnetic and magnetocaloric data.

1. Introduction

The investigation in magnetic hysteresis is shared by researches with an impressive variety of different backgrounds. Basically, the magnetic hysteresis comes from the fact that the system is trapped in local free energy minima and cannot easily achieve thermodynamic equilibrium. From theoretical and practical point of view there is widespread interest for hysteresis model. In particular, we are concerned with giant magnetocaloric materials, which present high entropy change induced by external magnetic field around first-order ferro-paramagnetic phase transition.

In this scope, materials that present first-order magnetic phase transition have attracted much attention since the discovery of the giant magnetocaloric effect (GMCE) in the $Gd_5Ge_2Si_2$ compound [1]. Later, several chemical Si–Ge substitutions in the system ($Gd_5(Ge_{(1-x)}Si_x)_4$) showed a variation on T_C from approximately 20 K ($x=0$) up to 276 K ($x=0.5$), and on the GMCE properties [2–4]. After that, other materials that present GMCE were discovered, such as: $LaFe_{11.4}Si_{1.6}$ [5]; MnAs [6]; $MnAs_{1-x}Sb_x$ ($0 \le x \le 0.3$) alloys [7,8]; $FeMn_{0.55}AsP_{0.45}$ [9,10] and $La(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds [11]. In general, the existence of a first-order transition in magnetic systems is associated with strong magnetoelastic coupling, such as the case of the magnetic materials cited above. The signature of the first-order transition is the existence of the thermal and magnetic hysteresis, which play an important role on the applicability of these materials in the magnetic refrigeration and on the comprehension of the GMCE. Furthermore, these aspects may be of interest for the understanding of others physical phenomena as the case of the barocaloric effect [12]. For these reasons, theoretical description of the influence of the magnetoelastic interaction on the magnetic hysteresis is of fundamental importance.

In this work, we elucidate part of this problem focusing on a simple system described by a model Hamiltonian, including exchange and magnetoelastic interactions in presence of an external magnetic field. The onset of the first-order magnetic phase transition, the hysteresis diagram and its application to the giant magnetocaloric material MnAs are discussed. MnAs is a ferromagnet with saturation magnetization of 3.5 μ_B. A first-order ferromagnetic to paramagnetic transition takes place at $T_C=$ 318 K. This transition is accompanied by a structural transition from hexagonal NiAs type to an orthorhombic MnP-type structure [6]. Our experimental data for temperature and magnetic field dependence of the magnetization as well as the magnetocaloric effect are in good agreement with the proposed model.

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2. Theory

The magnetic properties in MnAs were investigated in the framework of the model Hamiltonian [13]:

$$\hat{H} = -\sum_{i,j}\gamma_{ij}\vec{J}_i\vec{J}_j - \sum_{i,j}\zeta_{ij}(\vec{J}_i\vec{J}_j)^2 - g\mu_B\mu_0 h\sum_i J_i^Z \quad (1)$$

The first term in (1) represents the exchange interaction, where γ_{ij} are the exchange parameters between pairs of magnetic ions. The biquadratic term describes the magnetoelastic interaction in the momentum operators framework [14] and is associated with the exchange striction in our model, ζ_{ij} are the magnetoelastic parameters. The last term represents the Zeeman interaction, where g is the Landè factor, μ_B the Bohr magneton and h is the applied magnetic field.

In the mean field approximation, considering the magnetic interactions between the z-first-neighbors with same exchange γ and magnetoelastic ζ energies, the Hamiltonian (1) per magnetic ion reads:

$$\hat{H} = -g\mu_B(\lambda M + DM^3 + \mu_0 h)J^Z, \quad (2)$$

where $\lambda = 2z\gamma/Ng^2\mu_B^2$, $D = 4z\zeta/N^3g^4\mu_B^4$ and $M = Ng\mu_B\langle J^Z\rangle$ are the effective exchange, magnetoelastic parameters and magnetization, respectively. N is the number of magnetic ions per unit-cell volume.

One can obtain the magnetic free energy per magnetic ion for the Hamiltonian (2), and it is given by:

$$G = -k_BT\ln\left[\frac{\sin h(((2J+1)/(2J))x)}{\sin h(x/2J)}\right], \quad (3)$$

where k_B is Boltzmann's constant, J is the total angular momentum and $x = \frac{g\mu_B J}{k_BT}h_{eff}$, ($h_{eff} = \mu_0 h + \lambda M + DM^3$). It is important to note that the relation (3) is a Gibbs free energy, see Ref. [15]. In order to obtain the thermal evolution of the magnetization, studying the minima of the free energy, we should include the magnetic work performed by the system on relation (3). Therefore, the free energy of the system is

$$\Phi = G + \int Mdh_{eff} + \Phi_0, \quad (4)$$

where, the second term on relation (4) represents the magnetic work. The last term, Φ_0, as usual, is a shift added to fix $\Phi = 0$ for $M = 0$.

$$\Phi = -k_BT\ln\left[\frac{\sin h(((2J+1)/(2J))x)}{\sin h(x/2J)}\right] + \frac{\lambda M^2}{2} + \frac{3DM^4}{4} + k_BT\ln\left[\frac{\sin h(((2J+1)/(2J))x_0)}{\sin h(x_0/2J)}\right], \quad (5)$$

where $x_0 = \frac{g\mu_B J\mu_0 h}{k_BT}$. One can easily show that, when Φ is minimized with respect to the magnetization, it reproduces the well known magnetic state equations [16,17]. Nevertheless, the usual self-consistent solution of the magnetic state equation does not supply both metastable and stable magnetization solutions of Φ needed to map the thermal and magnetic hysteresis. Therefore, a careful investigation of local and global minima in our free energy Φ should be taken into account.

3. Application

Depending on the input model parameters, λ and D, a first-order magnetic transition can be obtained. Actually, for a given λ, there is a critical parameter D_c, for which $D > D_c$ and the system changes from a second-order to a first-order magnetic phase transition. If the system presents a second-order magnetic phase transition, then Φ will exhibit at most three critical points and the only possible metastability is induced by the magnetic field. However, when the system presents a first-order magnetic phase transition, Φ can exhibit five critical points, which may give rise to metastabilities leading to thermal and magnetic hysteresis.

The model parameters used for MnAs compound were obtained fitting experimental data for the magnetic hysteresis at 324 K and the thermal hysteresis with a magnetic field of 1 T. The saturation magnetization per μ_B is $gJ = 3.5$ [18]. The model parameters for Fig. 1 are $\lambda = 1130.92\ \mathrm{T^2/meV}$, $D = 21.75\times10^3\ \mathrm{T^4/meV^3}$, $g = 2.33$ and $J = 3/2$. These results are shown in Fig. 1a and b. Fig. 1a shows the M vs. $\mu_0 h$ at 324 K and the arrows indicate increasing or decreasing field processes. Fig. 1b shows the M vs. T for $\mu_0 h = 1$ T. The magnetization below the hysteresis region fits almost perfectly the experimental data (symbols), although the magnetization in the

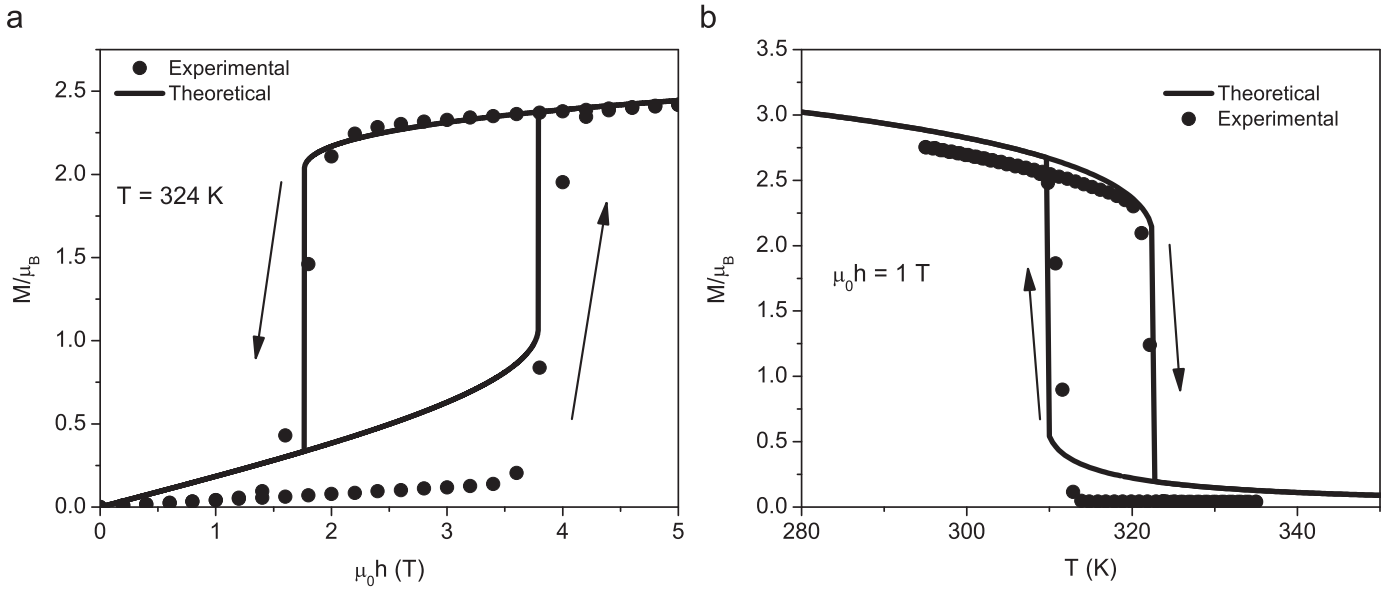

Fig. 1. (a) Magnetization in function of the applied magnetic field for 324 K for the MnAs compound. (b) Magnetization in function of the temperature for a field of 1 T for the MnAs compound. Lines are the theoretical results and circles are the experimental data [19]. The model parameter for both figures are $g = 2.33$, $J = 1.5$, $\lambda = 1130.92\ \mathrm{T^2/meV}$ and $D = 21.75\times10^3\ \mathrm{T^4/meV^3}$.