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Influence of modified surface effects on the magnetocaloric properties of ferromagnetic thin films

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ABSTRACT

We have studied the influence of surface effects on the magnetocaloric properties of ferromagnetic thin films. Using the effective field theory, we have computed the refrigerant capacity, isothermal entropy change, and the magnetic phase transition temperature as functions of the film thickness, and surface exchange coupling. We have shown that reduced and enhanced surfaces due to the presence of modified surface exchange couplings may drastically affect the magnetocaloric properties of the system. According to our results, in contrast to the conventional bulk ferromagnetic materials, depending on the film thickness and surface exchange coupling strength, maximal entropy change in thin film systems can be observed at temperatures well below the magnetic phase transition temperature. This observation can be beneficial from view point of technological applications.

1. Introduction

When a magnetic material is exposed to an externally applied magnetic field around its critical temperature, it may either heat up or cool down under adiabatic conditions. This behavior is called magnetocaloric effect (MCE) [1–7], and it has very high potential in technological [8–10], as well as biomedical [11] applications. For instance, the magnetic materials with advanced magnetocaloric properties can be used in magnetic refrigeration systems. On the other hand, MCE can also be utilized in medical treatment of malignant cells. For promising candidate materials, interaction of the system with the externally applied magnetic field causes a significant variation in the magnetic entropy in the vicinity of the magnetic phase transition temperature. Therefore, in terms of technological applications, the magnetic materials with critical temperature located around the room temperature are highly desired.

The total entropy of a magnetic material can be written as

$$S_{tot}(T, H) = S_L(T, H) + S_e(T, H) + S_M(T, H), \quad (1)$$

where the first term represents the contributions coming from the lattice vibrations (Debye part), the second term corresponds to the electronic contribution (Sommerfeld term), and the last term stands for the magnetic part. Under adiabatic conditions, total entropy defined by Eq. (1) should remain unchanged. In this regard, by applying a magnetic field towards the increasing field direction, the magnetic dipole moments of the material tend to align with each other which results in increasing magnetic order, and decreasing magnetic entropy. In this case, in order to keep the total entropy of the system unaltered, lattice and electronic entropy contributions increase, and the material heats up. The generated heat can be removed from the system by using a transfer fluid. This mechanism can be used for heating applications. On the other hand, as the applied magnetic field gradually decreases then the magnetic order also decreases, and the magnetic entropy becomes enhanced. This causes a decrement in the lattice and electronic entropy contributions. Consequently, the material cools down. As in the first cycle (i.e. the heating cycle), a transfer fluid can be used to benefit from this temperature drop. Therefore, the outcome of the process can be used in magnetic refrigeration systems [12].

In principal, MCE can be measured indirectly by calculating the magnetic contribution to the isothermal entropy change $\Delta S_M(T,H)$ or the adiabatic temperature variation $\Delta T_{ad}(T,H)$ according to [9]

$$\Delta S_M(T, H) = \int \left(\frac{\partial M}{\partial T}\right)_H dH, \quad \Delta T_{ad}(T, H) = -\int \frac{T}{C_x}\left(\frac{\partial M}{\partial T}\right)_H dH, \quad (2)$$

where $|\Delta S_M(T,H)|$ exhibits a prominent peak at the magnetic phase transition temperature. Hence, the MCE is maximized at the ferromagnetic-paramagnetic phase transition temperature. Mukherjee et al. [13] recently showed that the Maxwell relation incorporates contributions from the spin degrees of freedom and potential lattice degrees of freedom into the isothermal entropy change. Therefore, we will use the notation $\Delta S(T,H)$ instead of $\Delta S_M(T,H)$ in the remainder of the paper. In case of ordinary ferromagnetic materials, since the magnetization decreases with increasing temperature, the sign of ΔS should be negative which is called the conventional MCE. However, several ferrimagnetic

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and antiferromagnetic systems may exhibit positive ΔS_M which is called the inverse MCE [14,15]. In addition to the magnetocaloric properties given by Eq. (2), one may also define the refrigerant capacity q

$$q = -\int_{T_1}^{T_2} \Delta S(T)_H dT, \tag{3}$$

which is a measure of the amount of heat that can be transferred from the cold end to the hot end (denoted by T_1 and T_2, respectively) in one thermodynamical cycle during the adiabatic process.

Up to now, MCE has been widely investigated for a wide variety of bulk materials from both experimental and theoretical points of view [12,16]. Nevertheless, the rare earth Gadolinium has been found to be the best elementary material exhibiting rather promising magnetocaloric properties [17] such as an adiabatic temperature change $\Delta T_{ad} = 14$ K in 7 T magnetic field [18,19]. Besides, the isothermal entropy change for this elementary material is $|\Delta S| = 6.1$ and 10.6 (in units of $Jkg^{-1}K^{-1}$) for magnetic fields 2 T and 5 T, respectively [20]. Moreover, it exhibits magnetic phase transition around the room temperature with $T_c = 294$ K [19]. Based on these features, Gd element seems to be the best fit for active magnetic refrigeration (AMR). However, as a result of low resource efficiency, fabrication and mass production of magnetic refrigeration systems using Gadolinium as raw material for refrigerant cannot be efficient due to its high cost. Hence, the subsequent efforts have been devoted to the research of new magnetic materials in forms of alloys and compounds [21–31]. For instance, $Gd_5Si_2Ge_2$ compound exhibits $\Delta S = 20$ $Jkg^{-1}K^{-1}$ upon variation of magnetic field from 0 to 5 T around 273 K temperature [32]. Brück et al. [22] studied $MnFeP_{1-x}As_x$, and found giant MCE for this material which is comparable to that obtained for $Gd_5Si_2Ge_2$. Moya et al. [24] observed inverse MCE comparable with giant MCE materials in Ni-Mn-Sn ferromagnetic Heusler alloy. Thanh et al. [26] studied MCE in MnFe(P,Si,Ge) compounds, and in relation to Ref. [22], they succeeded in replacing As atoms by (Ge,Si) without losing favorable magnetic properties. From the theoretical point of view, there also exists a major literature regarding the modeling of MCE in a large class of magnetic systems [33–50], and a number of important results can be underlined as follows: Nóbrega et al. [41] used Monte Carlo (MC) simulation method to calculate the MCE in compounds $Gd_5Si_xGe_{1-x}$ for $x > 0.5$ where the material exhibits second order phase transition. de Oliveira and von Ranke [43] showed that around the first order phase transitions, the Maxwell relations defined in Eq. (2) are not valid. Ma and Du [44], performed MC simulations of binary alloy $Gd_{1-x}C_x$ with different concentrations of C atoms. They found that the magnetic phase transition temperature increases with increasing concentration of C atoms. Szalowski and Balcerzak [36] observed inverse MCE in a magnetic multilayer system with AF interplanar coupling which is related to the presence of compensation phenomena. Inverse MCE has also been recently observed by žukovič and Bobák [37] in a frustrated spin-1 Blume-Capel model on a triangular lattice. Finally, Arai et al. [46] used MC simulations and a Potts-like model to study the MCE in a Gd-R (R = Y,Zr) alloy, and they observed a good agreement between theoretical calculations and experimental observations.

The aforementioned works have been carried out for bulk materials. However, in contrast to the bulk systems, finite systems such as thin magnetic films may exhibit substantially peculiar magnetic properties due to their reduced coordination number at the surface. On the other hand, nowadays, it is possible to realize magnetic thin films even in the mono-layer limit by using advanced experimental techniques such as ultra-high vacuum and molecular beam epitaxy. Hence, the research of thin film magnetism has been growth rapidly in the last decades from both theoretical and experimental points of view [51–56]. Despite the technical difficulties which may be encountered in experimental realizations [57], and the limited number of studies dealing with MCE in thin film systems, the magnetic transition temperature and other magnetocaloric properties of potential MCE materials can be tailored by application of nanoscience to magnetocalorics [58]. Based on these facts, investigation of MCE in magnetic thin films offers rich physical phenomena. Previously, Morelli et al. [59] became the first group to conduct experimental studies on MCE in thin film systems by studying the magnetocaloric properties of doped lanthanum manganite films using the metalorganic decomposition technique. Mukherjee et al. [60], theoretically and experimentally investigated the tuning of magnetocaloric properties of Co/Cr superlattices for near room-temperature refrigeration applications. Miller et al. [61], studied Gd/W thin film heterostructures, and measured the entropy change peaks at a temperature of 284 K. The relative cooling power of the system was found to be somewhat lower than that of bulk Gd. In a recent work [62], large magnetocaloric effect in CrO_2/TiO_2 epitaxial films above room temperature were also reported. Theoretically, giant magnetocaloric effect were predicted for Dy [63], Tb [64], and Ho [65] based thin film structures.

As stated in Ref. [41], mean field theory (MFT) cannot explain the experimental behavior of magnetic specific heat around the critical temperature. Hence, in the present work, we aim to investigate the magnetocaloric properties of magnetic thin films using effective field theory (EFT) which presents numerical results quite superior to conventional MFT. Introduced by Kaneyoshi [66], this method partially takes into account the thermal fluctuations whereas MFT neglects all spin-spin correlations. Therefore, the results obtained by EFT are expected to be physically more realistic than the MFT calculations. The remaining parts of this paper can be summarized as follows: In Section 2, we present our model and related basic formalism. Section 3 is devoted to our numerical results and discussions. Finally, Section 4 contains our conclusions.

2. Model and formulation

Our system can be modeled as a layered magnetic structure which consists of ferromagnetic L monolayers (Fig. 1). The Hamiltonian can be written as

$$\mathscr{H} = -\sum_{<i,j>} J_{ij} S_i S_j - H \sum_i S_i \tag{4}$$

where the first term represents the nearest neighbor interactions with the ferromagnetic exchange coupling J_{ij}, and the second summation which is carried out over all the lattice sites denotes the Zeeman energy term. The local spin variable can take values $S_i = \pm 1$. If the neighboring spins are located in the surface region, we have $J_{ij} = J_s$, otherwise (i.e. except the bottom and the top surfaces of the film) $J_{ij} = J_b$.

Following the standard EFT procedure [67], the longitudinal magnetization $m_i = \langle S_i \rangle (i = 1,\ldots,L)$ of each layer can be given by the coupled nonlinear system of equations which are obtained by differential operator technique, and decoupling approximation [66,68]

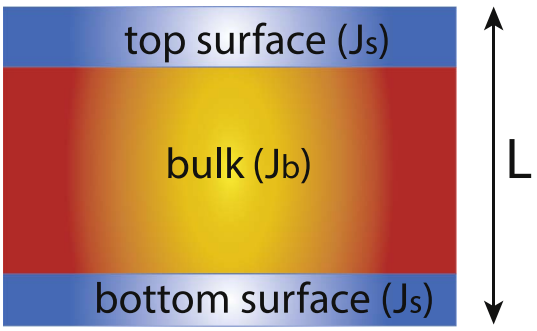

Fig. 1. Schematic representation of a ferromagnetic thin film composed of L distinct monolayers. The bottom and top surfaces have monolayer thickness. Surface spin-spin interaction is denoted by J_s. Bulk region thickness is $L - 2$ with exchange coupling J_b.