Magnetic properties and magnetocaloric effect in double Sr_2FeMoO_6 perovskites

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ABSTRACT

The magnetic properties and magnetocaloric effect in Sr_2FeMoO_6 compound have been studied using the Monte Carlo simulation. Thermal magnetization and dM/dT of Sr_2FeMoO_6 are given. The Curie temperatures $T_C(K)$ have been obtained. The temperature dependence of the magnetic entropy for a several magnetic field have been also obtained. The field dependence of relative cooling power and magnetic hysteresis cycle of Sr_2FeMoO_6 have been determined for a several magnetic field and temperatures. The Sr_2FeMoO_6 might be a promising base for developing the new kinds of magnetic refrigerant as working materials in magnetic refrigeration technology.

1. Introduction

Ordered double perovskite oxides of the general formula, $A_2BB'O_6$, have been known for several decades to have interesting magnetic properties and have drawn great scientific interest due to their high potential for novel spintronics. Especially, the magnetic and resistive properties of the double perovskite Sr_2FeMoO_6 are excellent for spintronic and magnetoresitive applications [1]. Kobayashi et al. [2], reported a large magnetoresistance effect with a fairly high magnetic transition temperature of about 418 K in Sr_2FeMoO_6, a material belonging to the class of double perovskites ($ABB'O_6$), where the alkaline-earth ion A is Sr and transition-metal ions B and B' are Fe and Mo arranged in a rock-salt structure, respectively [3]. Magnetism testing results show that the sample Sr_2FeMoO_6 is ferromagnetic with the magnetic transition temperature of about 380 K [4]. The double perovskite crystal structure consists of two interpenetrating face-centered-cubic sublattices. An ordered arrangement of Fe^{3+} ($3d^5$) and S = 5/2 magnetic moments antiferromagnetically coupled to the Mo^{5+} ($4d^1$) and S = 1/2 moments gives a total saturation magnetic moment of 4 μ_B at low temperature [5,6]. The Fe ions present a fairly ionic Fe^{3+} ($3d^5$) valence, whereas the Mo ions are in a strongly covalent Mo^{5+} ($4d^1$) state [7]. The polarization hysteresis loops of $Bi_{4-x}Sb(La)_xTi_3O_{12}$ have been given [8,9]. The magnetic properties and half-metallicity of the CaMnO_3/BaTiO_3 superlattice are investigated by employing the first-principle calculation based on density functional theory [10] and n Monte Carlo simulation is used to study the hexagonal prismatic nanoparticle consisting of a ferromagnetic core of spin-1 surrounded by a ferromagnetic shell of spin-3/2 with ferrimagnetic interface exchange coupling [11].

In other hand the ordered double-perovskite Sr_2FeMoO_6 possesses remarkable room-temperature low-field colossal magnetoresistivity and transport properties which are related, at least in part, to combined structural and magnetic instabilities that are responsible for a cubic-tetragonal phase transition near 420 K [12]. The latter condition is proving problematic: the substitution of other 3d metals for Fe^{3+} can give rise to the formation of an M^{2+}/Mo^{6+} ion pair [13–15]. Moreover, the magnetic properties of Sr_2FeMoO_6 ceramics obtained by sol–gel and solid state reaction methods and sintered by the classical method were compared with those of Sr_2FeMoO_6 ceramics obtained by the same two methods, but sintered by the spark plasma sintering technique [16] and neutron diffraction and magnetic susceptibility has been also used to study the crystalline and magnetic structures of Sr_2FeMoO_6 by Refs [17,18]. The density-functional theory, the effect of biaxial mechanical strain on the magnetic properties of double perovskite oxide Sr_2FeMoO_6 has been studied [19]. The saturation magnetization originating mainly from the Fe moments is correlated with the amount of Mo magnetic

moments observed by nuclear magnetic resonance measurements in Sr_2FeMoO_6 [20,21]. The magnetic double perovskites with the general formula $A_2BB'O_6$ (A = alkaline-earth-metal or rare earth metal cations and B, B = transition metal cations) have been extensively studied due to their interesting physical properties [22]. The key requirement of magnetic refrigeration is to have proper magnetocaloric materials, which can produce a large magnetic entropy change and a good magnetic reversibility at low magnetic fields and with a wide temperature range [23,24].

The paper is organized as follow. Section 2 present the Model, sections 3 and 4 present the Monte Carlo simulations and results and discussion, respectively and finally we have given in section 5 the conclusions.

2. Model and formulation

In this section, for explanation of Monte Carlo algorithm, a following Hamiltonian described the Sr_2FeMoO_6 compound using Ising model includes first and second nearest-neighbor interactions and external magnetic field h is used:

$$H = -J_{1(FeFe)} \sum_{<i,j>} S_i S_j - J_{2(FeFe)} \sum_{<<i,k>>} S_i S_k - J_{1(FeMo)} \sum_{<i,l>} S_i \sigma_l$$
$$- J_{2(FeMo)} \sum_{<<i,m>>} S_i \sigma_m -$$
$$J_{1(MoMo)} \sum_{<m,n>} \sigma_m \sigma_n - J_{2(MoMo)} \sum_{<<m,p>>} \sigma_m \sigma_p - h \left(\sum_i S_i + \sum_l \sigma_l \right) \quad (1)$$

where $S_i(Fe^{3+}) = 5/2$ and $\sigma_i(Mo^{5+}) = 1/2$ denotes the spin states of i-th cell. The ($<i, j>$, $<i, l>$ and $<m, n>$) and ($<<i, k>>$, $<<i, m>>$ and $<<m, p>>$) stand for the first and second nearest neighbor sites ((i and j), (i and l) and (m and n)) and ((i and k), (i,m) and (m,p)), respectively. The ($J_{1(FeFe)}$, $J_{1(FeMo)}$ and $J_{1(MoMo)}$ and ($J_{2(FeFe)}$, $J_{2(FeMo)}$ and $J_{2(MoMo)}$) are the first and second exchange interactions such as shown in Fig. 1. We will select $J_{1(FeMo)} = +20.0$ K, $J_{2(FeMo)} = +19.5$ K, $J_{1(FeFe)} = +17.0$ K, $J_{2(FeFe)} = +16.5$ K, $J_{1(MoMo)} = +16.0$ K and $J_{2(MoMo)} = +15.5$ K as a unit for performing calculations.

3. Monte Carlo simulations

The Sr_2FeMoO_6 compound is assumed to reside in the unit cells and the system consists of the total number of spins N = $N_S(Fe) + N_\sigma(Mo)$ with $N_S = 2331$ and $N_\sigma = 2310$. The Monte Carlo simulation is applied to simulate the Hamiltonian given by Eq. (1). In this section, we have used the cyclic boundary conditions on the lattice of Sr_2FeMoO_6 compound. The Monte Carlo update was performed by choosing random spins and then flipped (from current state $S_i(\sigma_i)$ to opposite state $-S_i(-\sigma_i)$) with Boltzmann based probability. In general, this can be done using the conventional Metropolis algorithm [25]. i.e. $P_{Metro} = \exp(-\Delta E/k_BT)$ where ΔE is the energy difference between the

Fig. 1. Crystal structure of double Sr_2FeMoO_6 perovskite.

before and the after flip. However, since the actual Metropolis suffers from large correlation time especially close to the critical point [26].

Our program calculates the following parameters, namely:
The internal energy per site E of Sr_2FeMoO_6 compound is;

$$E = \frac{1}{N} \langle H \rangle \quad (2)$$

The magnetization of Fe^{3+} and Mo^{5+} in Sr_2FeMoO_6 compound are, respectively:

$$M_S = \left\langle \frac{1}{N_S} \sum_i S_i \right\rangle \quad (3)$$

$$M_\sigma = \left\langle \frac{1}{N_\sigma} \sum_i \sigma_i \right\rangle \quad (4)$$

The total magnetization of Sr_2FeMoO_6 compound is:

$$M = \frac{N_S M_S + N_\sigma M_\sigma}{N_S + N_\sigma} \quad (5)$$

The magnetic specific heat of Sr_2FeMoO_6 compound is given by:

$$C_m = \frac{\beta^2}{N} (\langle E^2 \rangle - \langle E \rangle^2) \quad (6)$$

where $\beta = \frac{1}{k_BT}$, T denotes the absolute temperature.

Magnetocaloric effect can be related to the magnetic properties of the material through a thermodynamic Maxwell relation

$$\left(\frac{\partial S}{\partial h} \right)_T = \left(\frac{\partial M}{\partial T} \right)_h \quad (7)$$

The magnetic entropy change of Sr_2FeMoO_6 can be calculated from this equation;

$$S(T, h) = \int_0^T \frac{C_m}{T'} dT' \quad (8)$$

The magnetic entropy change between h different to zero and $h = 0$ is:

$$\Delta S_m(T, h) = S_m(T, h) - S_m(T, 0) = \int_0^{h_{max}} \left(\frac{\partial M}{\partial T} \right)_{h_i} dh_i$$
$$= \sum_i \left(\frac{\partial M}{\partial T} \right)_{h_i} \Delta h_i \quad (9)$$

$S_m(T,h)$ and $S_m(T,0)$ are the total entropy in presence and absence of magnetic field, respectively and h_{max} is the maximum applied external magnetic field. $\left(\frac{\partial M}{\partial T} \right)_{h_i}$ is the thermal magnetization for a fixed magnetic field h_i.

The defined parameter of relative cooling power (RCP) described as an area under the dependence of $\Delta S_m(T)$ on temperature, is a compromise between the magnitude of the magnetic entropy change and the width of the peak. The expression of relative cooling power RCP is:

$$RCP = \int_{T_c}^{T_h} \Delta S_m(T) dT \quad (10)$$

where T_c and T_h are the cold and the hot temperatures corresponding to both ends of the half-maximum value of ΔS_m^{max}, respectively.

The excitation magnetic field B is given by:

$$B = h + 4\pi M \quad (11)$$

4. Results and discussion

For the perfect SFMO case, we consider the experimental tetragonal cell within the I 4/mmm space group, with the lattice parameters a = 5.58 Å and c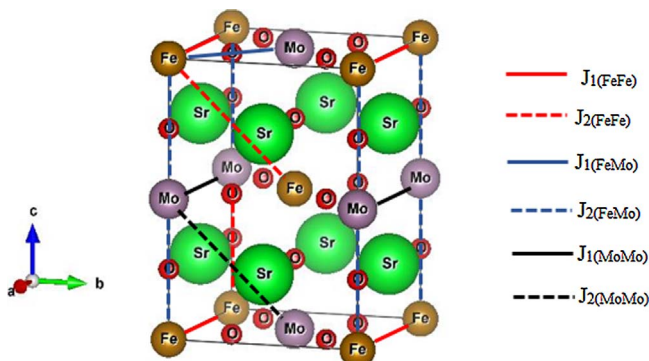 = 7.90 Å [27] containing two formula units (fu) (see