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ORIGINAL PAPER

Magnetocaloric Effect of Perovskite $Eu_{0.5}Sr_{0.5}CoO_3$

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Abstract Magnetocaloric properties of the $Eu_{0.5}Sr_{0.5}CoO_3$ system near a phase transition from a ferromagnetic to a paramagnetic state are investigated. It is shown that the magnetic entropy change (ΔS_M) peak spanning over a broad range of temperature leads to a remarkably wide working temperature region, yielding a significant performance in terms of refrigerant efficiency. Moreover, ΔS_M distribution is very uniform, which is desirable for Ericsson-cycle magnetic refrigerator. $Eu_{0.5}Sr_{0.5}CoO_3$ can be used as a working material of an apparatus based on the active magnetic regenerator cycle that cools hydrogen gas.

Keywords Magnetocaloric effect · Magnetic entropy change · Heat capacity change

1 Introduction

The refrigeration technology, based on the magnetocaloric effect (MCE) or electrocaloric effect, has been demonstrated as a promising alternative technology to classical refrigeration (air conditioning, refrigeration, liquefaction of gases, etc.) and has a great potential to compete successfully with compression and relaxation of the gases for refrigeration [1–12]. This refrigeration provides an efficient and environment-friendly solution to cooling. It is more efficient, inexpensive, and environmentally friendly for replacing the current refrigerators using greenhouse gases that are harmful to environment and contributing to global warming.

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In principle, magnetic refrigeration is based on the magnetocaloric effect, which is the thermal response of a magnetic solid to the variation of a magnetic field in an adiabatic process.

Perovskite-related cobalt oxides $Ln_{1-x}M_xCoO_3$ (Ln: lanthanides, M: alkaline-earth metals) have attracted much interest because of the existence of spin-state transitions and the unusual magnetic properties they exhibit [13].

In this paper, theoretical work on magnetization versus temperature in different magnetic fields for the $Eu_{0.5}Sr_{0.5}CoO_3$ is presented. A phenomenological model for simulation of magnetization dependence on temperature variation is used to predict magnetocaloric properties such as magnetic entropy change, heat capacity change, temperature change, and relative cooling power.

2 Theoretical Considerations

According to the phenomenological model [14], the dependence of magnetization on variation of temperature and Curie temperature T_c is represented by

$$M = \left(\frac{M_i - M_f}{2}\right)\left[\tanh\left(A(T_C - T)\right)\right] + BT + C, \qquad (1)$$

where M_i is an initial value of magnetization at ferromagnetic–paramagnetic transition, and M_f is a final value of magnetization at ferromagnetic–paramagnetic transition as shown in Fig. 1, where $A = \frac{2(B-S_c)}{M_i - M_f}$, B is the magnetization sensitivity $\frac{dM}{dT}$ at ferromagnetic state before transition, S_c is the magnetization sensitivity $\frac{dM}{dT}$ at Curie temperature T_C, and $C = (\frac{M_i + M_f}{2}) - BT_C$.

Equation (1) is determined by the physical mechanism that the magnetic moments can be increased by decreasing

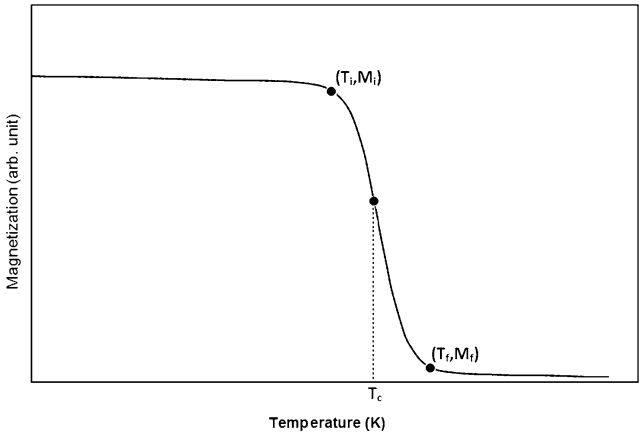

Fig. 1 Temperature dependence of magnetization in constant applied field

the temperature. At temperatures well below the Curie point, the electronic magnetic moments of a ferromagnetic specimen are essentially all lined up, when regarded on a microscopic scale.

A magnetic entropy change of a magnetic system under adiabatic magnetic field variation from 0 to final value $H_{\max}$ is available by

$$\Delta S_M = \left(-A\left(\frac{M_i - M_f}{2}\right)\operatorname{sech}^2\big(A(T_C - T)\big) + B\right)H_{\max}. \tag{2}$$

The foundation of large magnetic entropy change is attributed to high magnetic moment and rapid change of magnetization at T_c. A result of Eq. (2) is a maximum magnetic entropy change $\Delta S_{\max}$ (where $T = T_C$), which can be evaluated as in the following equation:

$$\Delta S_{\max} = H_{\max}\left(-A\left(\frac{M_i - M_f}{2}\right) + B\right). \tag{3}$$

Equation (3) is an important equation for taking into consideration the value of the magnetic entropy change to evaluate magnetic cooling efficiency with its full-width at half-maximum.

A determination of full-width at half-maximum δT_{FWHM} can be carried out as follows:

$$\delta T_{\mathrm{FWHM}} = \frac{2}{A}\cosh^{-1}\left(\sqrt{\frac{2A(M_i - M_f)}{A(M_i - M_f) + 2B}}\right). \tag{4}$$

This equation gives a full-width at half-maximum magnetic entropy change contributing for estimation of magnetic cooling efficiency as follows. The magnetic cooling efficiency is estimated by considering the magnitude of magnetic entropy change ΔS_M and its full-width at half-maximum (δT_{FWHM}). The product of $-\Delta S_{\max}$ and δT_{FWHM} is called the relative cooling power (RCP) based on magnetic entropy change:

$$\begin{aligned}\mathrm{RCP} &= -\Delta S_M(T, H_{\max}) \times \delta T_{\mathrm{FWHM}} \\ &= \left(M_i - M_f - 2\frac{B}{A}\right)H_{\max} \\ &\quad \times \cosh^{-1}\left(\sqrt{\frac{2A(M_i - M_f)}{A(M_i - M_f) + 2B}}\right).\end{aligned} \tag{5}$$

The magnetization-related change of the specific heat is given by

$$\Delta C_{P,H} = T\frac{\delta \Delta S_M}{\delta T}. \tag{6}$$

According to this model [14], $\Delta C_{P,H}$ can be rewritten as

$$\begin{aligned}\Delta C_{P,H} &= -TA^2(M_i - M_f)\operatorname{sech}^2\big(A(T_C - T)\big) \\ &\quad \times \tanh\big(A(T_C - T)\big)H_{\max}.\end{aligned} \tag{7}$$

A temperature change of a magnetic system under adiabatic magnetic field variation from 0 to $H_{\max}$ can be written in the form

$$\begin{aligned}\Delta T &= -\frac{T}{C_P}\int_0^{H_{\max}}\left(\frac{\partial M}{\partial T}\right)_E dH, \\ &= \frac{AT(M_i - M_f)}{2C_P}\big[\operatorname{sech}^2\big(A(T_C - T)\big) + B\big]H_{\max},\end{aligned} \tag{8}$$

C_p is a heat capacity per mole at constant magnetic field.

From this phenomenological model one can easily assess the values of δT_{FWHM}, $|\Delta S|_{\max}$, RCP, and ΔT for $Eu_{0.5}Sr_{0.5}CoO_3$ under magnetic field variation.

3 Theoretical Work

To evaluate the magnetocaloric effect in $Eu_{0.5}Sr_{0.5}CoO_3$, a series of numerical calculations were made around the ferromagnetic transition with parameters as displayed in Table 1. A heat capacity $C_p = 550$ J/kg K for $Eu_{0.5}Sr_{0.5}CoO_3$. Figure 2 shows the magnetization versus temperature in different applied magnetic fields for $Eu_{0.5}Sr_{0.5}CoO_3$. The symbols represent experimental data from Ref. [15], while the dashed curves represent the modeled data using the model parameters given in Table 1. It is seen that for the given parameters, the results of calculation are in a good agreement with the experimental results. Furthermore, Figs. 3–5 show the temperature dependence of change of the magnetic entropy, specific heat, and temperature, respectively, subject to different applied field changes. A peak in the entropy change ($\Delta S_{\max}$) occurs near T_C in each applied field change.

Table 1 Model parameters for $Eu_{0.5}Sr_{0.5}CoO_3$ in different applied magnetic fields

H (T)	M_i (emu g^{-1})	M_f (emu g^{-1})	T_c (K)	B (emu g^{-1} K^{-1})	S_c (emu g^{-1} K^{-1})
0.1	13.45	0.95	136	−0.025	−0.70
0.5	17.71	1.97	142	−0.020	−0.40
4	28.08	4.07	154	−0.013	−0.27

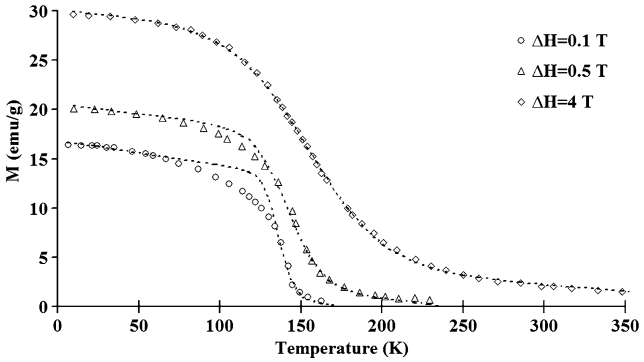

Fig. 2 Magnetization in different applied magnetic fields for the $Eu_{0.5}Sr_{0.5}CoO_3$ versus temperature. The *dashed curves* are modeled results, and *symbols* represent experimental data from Ref. [15]

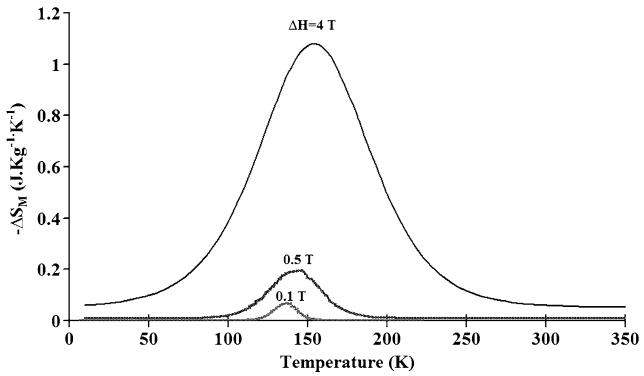

Fig. 3 Magnetic entropy change as function of temperature for $Eu_{0.5}Sr_{0.5}CoO_3$ in different applied magnetic field shifts

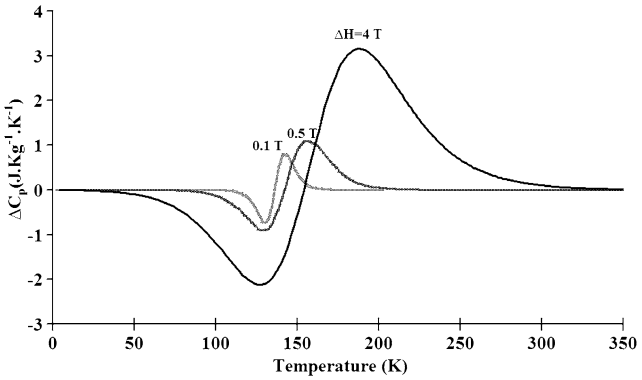

Fig. 4 Heat capacity changes as functions of temperature for $Eu_{0.5}Sr_{0.5}CoO_3$ in different applied magnetic field shifts

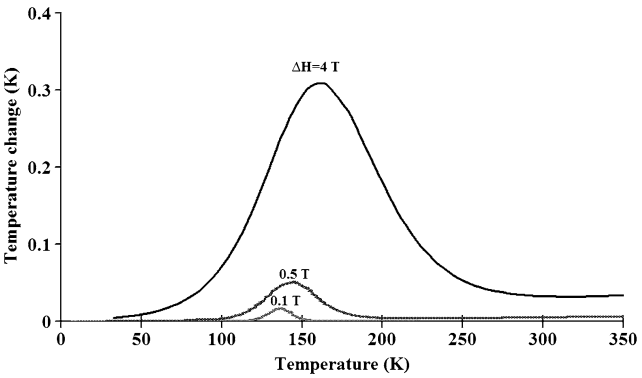

Fig. 5 Temperature changes as functions of temperature for $Eu_{0.5}Sr_{0.5}CoO_3$ in different applied magnetic field shifts

The values of maximum magnetic entropy change, full-width at half-maximum, and relative cooling power at different magnetic fields for $Eu_{0.5}Sr_{0.5}CoO_3$ are calculated by using Eqs. (3)–(5), respectively, and tabulated in Table 2. Furthermore, the maximum and minimum values of specific heat change for each sample are determined from Fig. 4.

Both ΔS_M and ΔT reflect a fundamental importance on the understanding of the behavior of the MCE, and these terms can be approximately estimated using Eqs. (2) and (8), respectively.

The largest entropy change value of 1.08 J/kg K occurs at $T = 154$ K for $\Delta H = 4$ T. The peaks broaden, increasing the working temperature range for devices and maintaining refrigeration capacity, a figure of merit in magnetocaloric materials that depend on both the height $-\Delta S_M$ and δT_{FWHM} of the peak. The RCP reached sizable value of 92.59 J/kg for $\Delta H = 4$ T. Moreover, ΔS_M distribution of the $Eu_{0.5}Sr_{0.5}CoO_3$ is uniform. This feature is desirable for an Ericsson-cycle magnetic refrigerator [16]. ΔT is presented in Fig. 5. ΔT undergoes an abrupt rise at T_C, and the temperature range of the large ΔT expanded with increasing magnetic field. Figure 5 indicates that the temperature range between 20 and 300 K can be covered using the $Eu_{0.5}Sr_{0.5}CoO_3$ system. $-\Delta S_M(T)$ peaks span over a wide temperature region, which can significantly improve the global efficiency of the magnetic refrigeration. To investigate more precisely this issue, the refrigerant capacity RC has been computed, which is considered to be the most important factor for assessing the usefulness of a magnetic

Table 2 The predicted values of applied magnetocaloric properties for $Eu_{0.5}Sr_{0.5}CoO_3$ in different applied magnetic field shifts

ΔH (T)	$-\Delta S_{\max}$ (J/kg K)	δT_{FWHM} (K)	RCP (J/kg)	$\Delta C_{P,H(\max)}$ (J/kg K)	$-\Delta C_{P,H(\min)}$ (J/kg K)	$\lvert\Delta T\rvert_{\max}$ (K)	RC (J/kg)
0.1	0.07	16.81	1.13	0.80	−0.73	0.02	0.94
0.5	0.20	38.07	7.48	1.10	−0.91	0.05	6.09
4	1.08	85.73	92.59	3.16	−2.12	0.31	74.06

refrigerant material. The RC values in Table 2 were derived from $\mathrm{RC} = \int_{T_C-\frac{\delta T_{\mathrm{FWHM}}}{2}}^{T_C+\frac{\delta T_{\mathrm{FWHM}}}{2}} \Delta S_M \, dT$ [17, 18].

When increasing ΔH, δT_{FWHM} increases up to 85.73 K for $\Delta H = 4$ T. Thus, in spite of a modest $\Delta S_{\max}$, the RC remains appreciable owing to the large δT_{FWHM} value.

The present Perovskite cobalt oxide $Eu_{0.5}Sr_{0.5}CoO_3$ has promising ΔT values for use as magnetic refrigerants. It can be used as a working material of an apparatus based on the active magnetic regenerator cycle that cools hydrogen gas from the temperature of liquid natural gas (112 K) to nearly the boiling point of hydrogen (20 K).

In conclusion, $Eu_{0.5}Sr_{0.5}CoO_3$ system near a phase transition from a ferromagnetic to a paramagnetic state shows good magnetocaloric properties. The $-\Delta S_M$ peak spanning over a broad range of temperature leads to a remarkably wide working temperature region, yielding a significant performance in terms of refrigerant efficiency. Moreover, ΔS_M distribution is very uniform, which is desirable for Ericsson-cycle magnetic refrigerator. $Eu_{0.5}Sr_{0.5}CoO_3$ can be used as a working material of an apparatus based on the active magnetic regenerator cycle that cools hydrogen gas.

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