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Magnetocaloric effect and critical behaviors of R_2NiMnO_6 (R=Eu and Dy) double perovskite oxides

Lei Su [a, b], Xiang-Qun Zhang [b], Qiao-Yan Dong [c, **], Ya-Jiao Ke [b], Kai-Yue Hou [b, c], Cheng-Shi Liu [a], Zhao-Hua Cheng [b, *]

[a] Key Laboratory for Microstructural Material Physics of Hebei Province, School of Science, Yanshan University, Qinhuangdao 066004, PR China
[b] Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, PR China
[c] Center for Condensed Matter & Beijing Key Laboratory of Metamaterials and Devices, Department of Physics, Capital Normal University, Beijing 100048, PR China

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ABSTRACT

We have investigated the magnetocaloric effects and critical behaviors of Eu_2NiMnO_6 and Dy_2NiMnO_6 double perovskite oxides. For a magnetic field varying from 0 to 7 T, the maximum values of the magnetic entropy change ($|\Delta S_M^{max}|$) reach 4.0 J/kg K and 5.2 J/kg K, and the relative refrigeration capacity (*RCP*) values are 241.5 J/kg and 385.1 J/kg for Eu_2NiMnO_6 and Dy_2NiMnO_6, respectively. The relatively high values of $|\Delta S_M|$ and *RCP* suggest that these double perovskite oxides can be used as candidates of magnetic refrigerants working in a wide temperature range. Various techniques such as modified Arrott plot, Kouvel-Fisher method and critical isotherm analysis are used to estimate the critical exponents (β, γ and δ) as well as T_C for Eu_2NiMnO_6. These critical exponents not only obey the Widom scaling relation $\delta = 1 + \gamma/\beta$, but also fulfill the scaling equation $M(H, \varepsilon) = \varepsilon^{\beta} f_{\pm}(H/\varepsilon^{\beta+\gamma})$ where $\varepsilon = (T - T_C)/T_C$, f_+ ($T > T_C$) and f_- ($T < T_C$) are the regular analytic functions. Therefore, the deduced critical exponents are reasonably accurate. Moreover, temperature variation in effective critical exponents resemble with those for disordered ferromagnet, which matches with the Griffiths-like phase behavior observed from inverse magnetic susceptibility just above T_C.

1. Introduction

In recent years, with the constantly increasing need for powerful, clean, efficient, and miniaturized devices incorporating different physical properties, much attention has been attracted to double perovskite oxides as multifunctional materials because they simultaneously possess magnetic, dielectric, magnetodielectric and magnetocaloric (MC) properties [1–5]. This kind of oxides have general stoichiometric formula $A_2B'B''O_6$, where A is rare-earth, alkali or alkaline-earth ion and B′, B″ are transition metal ions [6]. La_2NiMnO_6 is a typical one of them. There are abundant reports on its magnetic and magnetocaloric properties [7,8], magnetodielectric properties [9], magnetocapacitance and magnetoresistance [10].

La_2NiMnO_6 shows a ferromagnetic (FM)-paramagnetic (PM) phase transition around Curie temperature (T_C) of 280 K [11]. Ni^{2+}–O–Mn^{4+} superexchange interaction leads to the appearance of FM state [12]. For magnetocaloric effect (MCE), Monte Carlo simulations have proved the temperature where the maximum of the magnetic entropy change locates is in accord with T_C [13]. Furthermore, modulating the coupling between the spin and phonon have greatly enhanced the magnetic entropy change of polycrystalline La_2NiMnO_6 [7].

On the basic of the magnetocaloric effect, magnetic refrigeration as a promising technology compared with the traditional gas-compression refrigeration because of its higher efficiency and environmentally friendly has attracted more attentions [14,15]. It is of great significance to explore new magnetic refrigeration materials. Recently, the double perovskite family of R_2NiMnO_6 (R = Pr, Nd, Tb, Ho, and Y) have been found they possess considerably high values of $|\Delta S_M|$ and RCP as the prospective magnetocaloric refrigerant around T_C [4]. Subsequently, Dy_2NiMnO_6 is also thought as a promising magnetic refrigerant material because it shows amazing

* Corresponding author.
** Corresponding author.
E-mail addresses: dongqy@cnu.edu.cn (Q.-Y. Dong), zhcheng@iphy.ac.cn (Z.-H. Cheng).

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magnetocaloric effect in a wide temperature range [16]. In addition, many Eu-based oxides such as $EuHo_2O_4$ and $EuDy_2O_4$ [17], $Eu_{1-x}Ba_xTiO_3$ ($0.1 \leq \times \leq 0.9$) [18], $EuTiO_3$ [19] have been reported to exhibit a large magnetic entropy change. Within this context, we report the magnetocaloric effect of R_2NiMnO_6 (R = Eu and Dy) polycrystalline samples. At the same time, we also systematically investigate the critical behavior of Eu_2NiMnO_6 for a better understanding of its magnetic transition.

2. Experimental process

Polycrystalline Eu_2NiMnO_6 and Dy_2NiMnO_6 were synthesized by standard solid-state reaction method. Stoichiometric amounts of R_2O_3 (R = Eu or Dy) (purity of 99.99 wt %), NiO (purity of 99.998%) and MnO_2 (purity of 99.9 wt %) were intensively mixed. The mixtures for Eu_2NiMnO_6 and Dy_2NiMnO_6 samples were calcined at 1000 °C for 24 h and 1200 °C for 24 h under the atmosphere of air, respectively. Then they were cooled down to room temperature in the furnace at the rate of 1 °C/min. Consecutively, the resulting powders were reground, pressed into pellets and sintered at 1200 °C for 24 h for Eu_2NiMnO_6 and at 1300 °C for 24 h for Dy_2NiMnO_6. Powder X-ray diffractometer (Rigaku Ultima-IV diffractometer with combined Cu-Kα radiation) was performed to characterize the crystal structure of the samples. The dc magnetic measurements were carried out on a superconducting quantum interference device magnetometer (MPMS XL, Quantum Design) in magnetic fields up to 7 T at temperatures between 2 K and 300 K.

3. Results and discussion

3.1. Structural properties

Rietveld refined powder X-ray diffraction (XRD) patterns of Eu_2NiMnO_6 and Dy_2NiMnO_6 polycrystalline samples at room temperature (See Fig. 1) show that the Eu_2NiMnO_6 sample is in pure phase with a monoclinic structure (space group $P2_1/n$), while Dy_2NiMnO_6 sample has the main phase with a monoclinic structure (space group $P2_1/n$) as well as a small amount of impurity phase Dy_2O_3 marked by "↓" in the pattern of Fig. 1. The obtained structural and reliability parameters of Eu_2NiMnO_6 and Dy_2NiMnO_6, as well as La_2NiMnO_6 [20,21], are shown in Table 1. The lattice parameters of Eu_2NiMnO_6 and Dy_2NiMnO_6 are in accord with the previous works [22,23]. As summarized in Table 1, lattice parameters a and c, cell volume v, and ⟨Ni–O–Mn⟩ bond angle ψ decrease, while lattice parameter b increases with decreasing the lanthanide ionic radius. Refinement parameter χ^2 is defined as R_{wp}/R_{exp}, where R_{wp} is the weighted-profile R value, R_{exp} is the statistically expected R value and reflects the quality of the data (*i.e.* the counting statistics) [24]. Ideally, χ^2 should approach 1. However, the χ^2 values of Eu_2NiMnO_6 and Dy_2NiMnO_6 polycrystalline samples are much larger than 1. There are two reasons. One is that the XRD data have been over-collected which results a small R_{exp} value. The other is a large R_{wp} value due to the level of background when collecting XRD data.

Table 1
Structural and reliability parameters obtained from the refinement for R_2NiMnO_6 (R = Eu and Dy) as well as La_2NiMnO_6 [20,21].

	La_2NiMnO_6	Eu_2NiMnO_6	Dy_2NiMnO_6
a (Å)	5.5115	5.3249	5.2466
b (Å)	5.4851	5.5282	5.5500
c (Å)	7.7387	7.5873	7.5055
V (Å^3)	232.79	223.35	218.55
β(°)	90.015(2)	90.008(1)	90.251(7)
Bond angles(°)			
Ni–O_1–Mn	157.6(1)	149.4(2)	143.2(7)
Ni–O_2–Mn	163.5(9)	145.0(3)	148.8(8)
Ni–O_3–Mn	160.9(1)	150.8(2)	149.4(6)
⟨Ni-O-Mn⟩	160.7(1)	148.4(2)	147.2(0)
Average bond length(Å)			
⟨Ni–O⟩	1.97(3)	2.01(2)	1.95(5)
⟨Mn–O⟩	1.96(2)	1.96(2)	2.00(4)
R:x	0.0021(6)	0.5108(9)	0.5168(3)
y	0.0171(2)	0.5590(1)	0.5692(5)
z	0.2524(7)	0.2483(8)	0.2517(3)
Ni:x y z	0 1/2 0	1/2 0 0	1/2 0 0
Mn:x y z	1/2 0 0	0 1/2 0	0 1/2 0
O_1:x	−0.218(5)	0.2257(9)	0.1901(4)
y	0.191(5)	0.2160(8)	0.1895(0)
z	−0.019(4)	0.9373(5)	0.9415(9)
O_2:x	0.233(4)	0.3238(8)	0.3140(0)
y	0.758(4)	0.6892(9)	0.7141(4)
z	0.466(3)	0.9582(1)	0.9509(3)
O_3:x	0.559(2)	0.4108(3)	0.4019(8)
y	−0.001(1)	0.9775(7)	0.9694(3)
z	0.265(3)	0.2698(0)	0.2551(3)
R_p	7.93	1.90	1.48
R_{wp}	10.8	2.95	2.04
χ^2	3.47	7.99	5.14

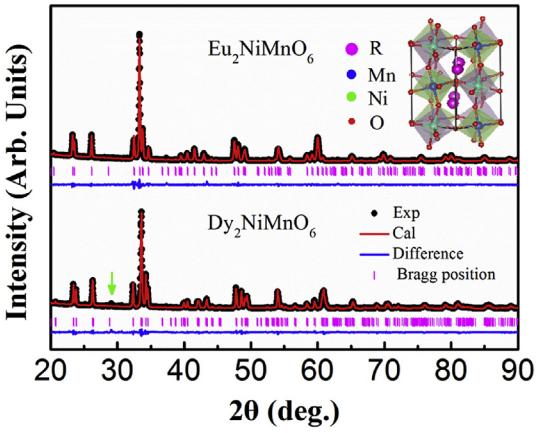

Fig. 1. Rietveld refined powder XRD patterns of Eu_2NiMnO_6 and Dy_2NiMnO_6 at room temperature. The experimental data are indicated by dots, and the calculated profile is shown by the solid line. The short vertical lines show the positions of the Bragg diffraction peak. The underneath curve shows the difference between the observed and calculated intensity. The inset shows the crystallographic structure of R_2NiMnO_6.

3.2. Magnetic properties

In order to confirm the magnetic properties of Eu_2NiMnO_6 and Dy_2NiMnO_6 oxides, the temperature (T)-dependence of magnetization (M) has been measured. Fig. 2(a)–(b) show the zero field cooling (ZFC) and field cooling (FC) magnetization *vs.* temperature curves of Eu_2NiMnO_6 and Dy_2NiMnO_6 from 2 K to 300 K under 0.01 T. With increasing the temperature, it is evident that the compounds undergo a ferromagnetic-paramagnetic phase transition. The Curie temperature T_C, corresponding to the maximum slope of FC M-T curve ($|dM/dT|$) (See the insets of Fig. 2(a)–(b), is determined to be 145 K for Eu_2NiMnO_6 and 97 K for Dy_2NiMnO_6, respectively. They are in agreement with the result reported in the literatures [22,23]. The T_C of La_2NiMnO_6 reported is 280 K [11]. Obviously, T_C shifts towards low temperature with decreasing the lanthanide ionic radius. It also can be seen from Fig. 2(a)–(b) that the ZFC and FC curves are completely reversible around T_C. However, a significant thermal magnetic irreversibility between the ZFC and FC branches is clearly observed below T_C. This kind of bifurcation is also yielded in many other R_2NiMnO_6 compounds such as