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INVESTIGATION ON MAGNETOCALORIC CHARACTERISTICS OF ROOM TEMPERATURE MAGNETIC REFRIGERATION MATERIALS GD, GDER AND GDDY

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ABSTRACT

By means of the de Gennes model, the magnetocaloric characteristics of Gd-R (R= Dy, Er) alloys as well as Gd, which are materials for sustainable energy, are investigated and the related theoretical and experimental results are compared. The effects of R-doped concentrations on the Curie temperature of Gd-R alloys are revealed. Furthermore, the dependencies of temperature of the heat capacities and adiabatic temperature changes of Gd, $Gd_{0.95}Dy_{0.05}$, and $Gd_{0.95}Er_{0.05}$ under 0 and 2T applied magnetic fields are analyzed and discussed. The calculated results shows that the Curie temperatures of these materials decrease with increasing R-doped concentration; the effect of magnetization/demagnetization on the adiabatic temperature change of Gd-R alloys is weak, but on the temperature at maximum adiabatic temperature change of Gd-R alloys is relatively evident. The calculation results in the present paper may provide some references for the parametric design of room temperature magnetic refrigerators that are energy conversion devices with environmental protection and energy saving.

Keywords: Magnetocaloric material; Curie temperature; Heat capacity; Adiabatic temperature change; Sustainable energy

NONMENCLATURE

Abbreviations	
MCE	magnetocaloric effect
Symbols	
$B_J(y)$	Brillouin function,
C_H	iso-magnetic field heat capacity, $\mathrm{J\,K^{-1}\,mol^{-1}}$
$\overline{g}$	effective Lander factor
g	Lander factor
H	magnetic field intensity, T
$\overline{J}$	effective angular moment number
k	Boltzmann constant, $\mathrm{J\,K^{-1}}$
M	magnetization, $\mathrm{A\,m^{-1}}$
N	number of magneton per unit volume
R	universal gas constant, $\mathrm{J\,mol^{-1}\,K^{-1}}$
$S(T,H)$	total entropy of a magnetic material, $\mathrm{J\,kg^{-1}\,K^{-1}}$
$S_E(T)$	electronic entropy, $\mathrm{J\,kg^{-1}\,K^{-1}}$
$S_L(T)$	lattice entropy, $\mathrm{J\,kg^{-1}\,K^{-1}}$
$S_M(T)$	magnetic entropy, $\mathrm{J\,kg^{-1}\,K^{-1}}$
T_D	Debye temperature, K
T	absolute temperature, K
x	molar fraction of component
Greek letters	
γ	specific heat coefficient of electron
$(\Delta T)_{ad}$	adiabatic temperature change, K
$\overline{\theta_c}$	Curie temperature, K
λ	molecular field coefficient
$\overline{\mu}$	effective magnetic moment
μ_B	Bohr magneton, $\mathrm{A\,m^2}$
μ_0	vacuum permeability, $\mathrm{F\,m^{-1}}$

1. INTRODUCTION

Ozone depletion and the greenhouse effect are great challenges of the environmental protection in the urban energy systems [1]. In order to overcome these difficulties, a number of scholars and engineers have been exploring some new refrigeration technologies. Magnetic refrigeration is an environmentally friendly refrigeration technology, which employs magneto-

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caloric materials as refrigerants based on the magnetocaloric effect (MCE) [2], and its refrigeration efficiency may attain 60% Carnot efficiency [3]. In spite of its high energy efficiency, small refrigeration capacity or narrow refrigeration temperature span restricts its commercialization [4]. Therefore, exploring new magnetic refrigeration materials with giant MCE and investigating magnetocaloric characteristic of MCE materials are extremely important contents [5]. Heavy-rare-earth elements and their alloys have generally high magnetic moments [6]. For instance, Gadolinium (Gd), a rare-earth metal with large MCE, is a most active magnetic refrigerant and has been adopted widely in the room-temperature magnetic refrigeration experimental machines [7]. In addition, the large or giant MCE has been found in several Gd-based alloys. For example, Pecharsky et al. [8] discovered $Gd_5Si_2Ge_2$ exhibiting the large MCE that is two times larger than Gd. Zimm et al. [9] built and demonstrated a permanent-magnet rotary magnetic refrigerator using Gd and Gd-Er alloy as the working substances. Okamura et al. [10] designed and operated a room-temperature rotary magnetic refrigerator employing $Gd_{0.92}Y_{0.08}$, $Gd_{0.84}Dy_{0.16}$, $Gd_{0.87}Dy_{0.13}$, and $Gd_{0.89}Dy_{0.11}$ as the working substances. These experimental machines show that magnetic refrigerators have an enormous potential to enter commercial markets [11], and further investigation on the magnetocaloric performances of magnetic refrigeration materials as Gd-based alloys is necessary.

In this paper, the magnetocaloric characteristics including the total entropy, the Curie temperature, and the adiabatic temperature change of Gd and Gd-R(R=Dy, Er) alloys are studied by means of de Gennes model. The effect of R-doped concentration on the Curie temperatures of Gd-R alloys is calculated and discussed. The temperature dependences of the heat capacity and adiabatic temperature change of Gd and $Gd_{0.95}Dy_{0.05}$, and $Gd_{0.95}Er_{0.05}$ are analyzed and evaluated under 0 and 2T applied magnetic fields.

2. *THERMODYNAMIC ANALYSIS OF SINGLE ELEMENT MAGNETIC MATERIAL*

For a single element ferromagnetic material, its magnetic entropy $S_M(T)$, lattice entropy $S_L(T)$, and electronic entropy $S_E(T)$ can be expressed as, respectively,

$$S_M(B,T) = R\left\{\ln\left[\frac{\sinh\left[y(2J+1)/2J\right]}{\sinh\left(y/2J\right)}\right] - yB_J(y)\right\} \quad (1)$$

$$S_L(T) = R\begin{bmatrix} -3\ln\left[1-\exp\left(-T_D/T\right)\right] \\ +12\left(T/T_D\right)^3\int_0^{T_D}\frac{x^3}{\exp(-x)-1}dx \end{bmatrix} \quad (2)$$

and

$$S_E(T) = \gamma T \quad (3)$$

where

$$B_J(y) = \coth\left[y(2J+1)/2J\right](2J+1)/2J - (1/2J)\coth\left[y/2J\right]$$

is the Brillouin function,

$$y = g\mu_B\mu_0 J\left(H+\lambda M\right)/kT \quad (4)$$

and satisfies the following state equation:

$$M = NgJB_J(y) \quad (5)$$

where M is the magnetization, k is the Boltzmann constant, R is the universal gas constant, γ is the specific heat coefficient of electron, T_D is the Debye temperature, T is the absolute temperature, N is the number of magneton per unit volume，g is the Lander factor, μ_B is the Bohr magneton, μ_0 is the vacuum permeability, λ is the molecular field coefficient, and H is the external magnetic field intensity. For given temperature and external magnetic field as well as other parameters, the magnetization M and y can be solved out through Eqs. (4) and (5).

Total entropy $S(T,H)$ of a magnetic material includes magnetic entropy $S_M(T,H)$, lattice entropy $S_L(T)$, and electronic entropy $S_E(T)$, i.e.,

$$S(T,H) = S_M(T,H) + S_L(T) + S_E(T) \quad (6)$$

Electronic entropy is always too small compared with lattice entropy or magnetic entropy to be considered in the following calculation. Thus, the iso-magnetic field heat capacity is given by

$$C_H = T(\frac{\partial S}{\partial T})_H = T(\frac{\partial S_M}{\partial T})_H + T(\frac{\partial S_L}{\partial T})_H \quad (7)$$

For a reversible adiabatic temperature change with magnetization or demagnetization, one has

$$S_M(H_0,T) + S_L(T) = S_M(H_1, T+\Delta T_{ad}) + S_L(T+\Delta T_{ad}) \quad (8)$$

According to above equations, the magnetic entropy, the lattice entropy, total entropy, magnetic heat capacity, lattice heat capacity, total heat capacity, and the adiabatic magnetization/demagnetization temperature change can be calculated.

3. *DE GENNES METHOD APPLYING TO BINARY ALLOYS*

Note that Eqs.(1)-(5) can be used to calculate only the entropy of the single element ferromagnetic material. For the binary alloys, such as those consisting of Gd and R (R=Dy, Er), we may introduce effective

Lander factor $\overline{g}$, effective angular moment number $\overline{J}$, effective magnetic moment $\overline{\mu}$ used in the de Gennes model. The related relationship for the Gd-R alloys are given by

$$\overline{G} = (\overline{g}-1)^2 \overline{J}(\overline{J}+1) = (1-x)G_{Gd} + xG_R \quad (9)$$

$$\overline{\mu}^2 = \overline{g}^2 \overline{J}(\overline{J}+1)\mu_B^2 = (1-x)\mu_{Gd}^2 + x\mu_R^2 \quad (10)$$

where x is the molar fraction of component R(R=Dy, Er) in binary alloy $Gd_{1-x}R_x$, G_{Gd} and G_R are the De Gennes factors, μ_{Gd} and μ_R are the effective magnetic moments of Gd and R respectively. And, $G_{Gd/R}$ and $\mu_{Gd/R}$ can be calculated through following equations:

$$G_{Gd/R} = (g_{Gd/R}-1)^2 J_{Gd/R}(J_{Gd/R}+1) \quad (11)$$

$$\mu_{Gd/R} = g_{Gd/R}\sqrt{J_{Gd/R}(J_{Gd/R}+1)}\mu_B \quad (12)$$

where $g_{Gd/R}$ is the Lander factor of Gd/R, $J_{Gd/R}$ is the angular quantum number of Gd/R. Based on Eqs. (9)-(12) and the basic data of Gd and R, $\overline{g}$, $\overline{J}$, and $\overline{G}$ as well as the Curie temperature $\overline{\theta_c}$ of $Gd_{1-x}R_x$ alloy can be calculated. For example, the Curie temperature of $Gd_{1-x}R_x$ can be obtained from the following equation [12]:

$$\overline{\theta_c} = 46.63\overline{G}^{2/3} \quad (13)$$

4. RESULTS AND DISCUSSION

Based on the related parameter values summarized in Table 1, the magnetocaloric characteristic of $Gd_{1-x}R_x$ (R=Dy, Er) is to be analyzed and discussed by numerical value method.

Table 1 Related parameter values of Gd, Dy, Er [12-15]

Material	Lander factor g	angular quantum number J	Debye temperature T_D(K)	Molar mass M_m (kg/mol)	density (kg/m^3)
Gd	2	3.5	173	0.157	7901
Dy	1.33	7.5	180	0.1625	8540
Er	1.2	7.5	230	0.167	9066

4.1.1 Effect of R-doped concentration x on the Curie temperature of $Gd_{1-x}R_x$

The Curie temperatures values of $Gd_{1-x}R_x$(R=Dy, Er) obtained from the theoretical calculation and experimental test are shown in Fig. 1. The calculated Curie temperatures versus R-doped concentration x curves for $Gd_{1-x}Dy_x$ and $Gd_{1-x}Er_x$ are, respectively, illustrated in solid and dotted lines. For comparison purpose, the measured Curie temperature values of Gd [16], $Gd_{0.88}Dy_{0.12}$[17], $Gd_{0.8}Dy_{0.2}$[18], $Gd_{0.73}Dy_{0.27}$[18], $Gd_{0.6}Dy_{0.4}$[18], $Gd_{0.5}Dy_{0.5}$[19], $Gd_{0.9}Er_{0.1}$[20], and $Gd_{0.84}Er_{0.16}$[21] are also shown in Fig.1. As shown the calculated results based on the De Gennes method are in good agreement with most of the experimental ones, especially as Gd, $Gd_{0.88}Dy_{0.12}$, $Gd_{0.8}Dy_{0.2}$, $Gd_{0.5}Dy_{0.5}$. Besides, the Curie temperatures $\overline{\theta_c}$ of the $Gd_{1-x}R_x$ (R=Dy, Er) alloys decrease linearly as R-doped concentration x increases. This means that the Curie temperature of the $Gd_{1-x}R_x$(R=Dy, Er) alloys can be adjusted through changing Dy or Er-doped concentration x. In the following section, some magnetocaloric performances of Gd, $Gd_{0.95}Dy_{0.05}$, and $Gd_{0.95}Er_{0.05}$, whose Curie temperatures are 293.0K, 287.5K, and 284.7K, respectively.

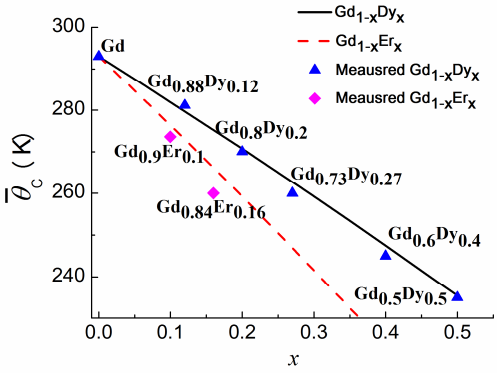

Fig.1. The Curie temperatures of $Gd_{1-x}R_x$(R=Dy, Er) versus R-doped concentration x curves.

4.1.2 The temperature dependency of heat capacity of $Gd_{1-x}R_x$

By using the related equations above, the heat capacity C_H of $Gd_{1-x}R_x$ (R=Dy, Er) versus temperature T with and without magnetic fields can be obtained, as shown in Fig. 2. As shown the heat capacities of Gd, $Gd_{0.95}Dy_{0.05}$, and $Gd_{0.95}Er_{0.05}$ approximately coincide at the absence of applied magnetic field when temperatures are below the Curie temperature of $Gd_{0.95}Er_{0.05}$, but they sharply drop down to around 24.5 J $K^{-1}mol^{-1}$ when the temperatures are higher than their corresponding Curie temperatures. For these materials, when the temperatures are higher than the Curie temperature of $Gd_{0.95}Dy_{0.05}$ or lower than the Curie temperature of Gd, the heat capacity of Gd is largest. But the heat capacities of these materials are almost same when temperatures are higher than the Curie temperature of Gd. This is because the magnetic heat capacity rapidly drops down to zero when temperatures are higher than the Curie temperature of these materials. Once the applied magnetic field is added,

there does not exists any rapid change of the heat capacities as that at the absence of applied magnetic field, as shown in Fig. 2(b). In this case, the heat capacity of $Gd_{0.95}Er_{0.05}$ is the largest in these three materials when temperatures are lower than 270K or so. The heat capacity of Gd is the largest in these three materials when temperatures are higher than 270K or so. The heat capacity of $Gd_{0.95}Dy_{0.05}$ is always between $Gd_{0.95}Er_{0.05}$ and Gd. In Fig. 2, triangles represent the experimental data, and circles represent another numerical result. As shown in Fig. 2(a), the calculation results in this paper has a similar trend with Ref. 22, but are different from those in Ref. 23.

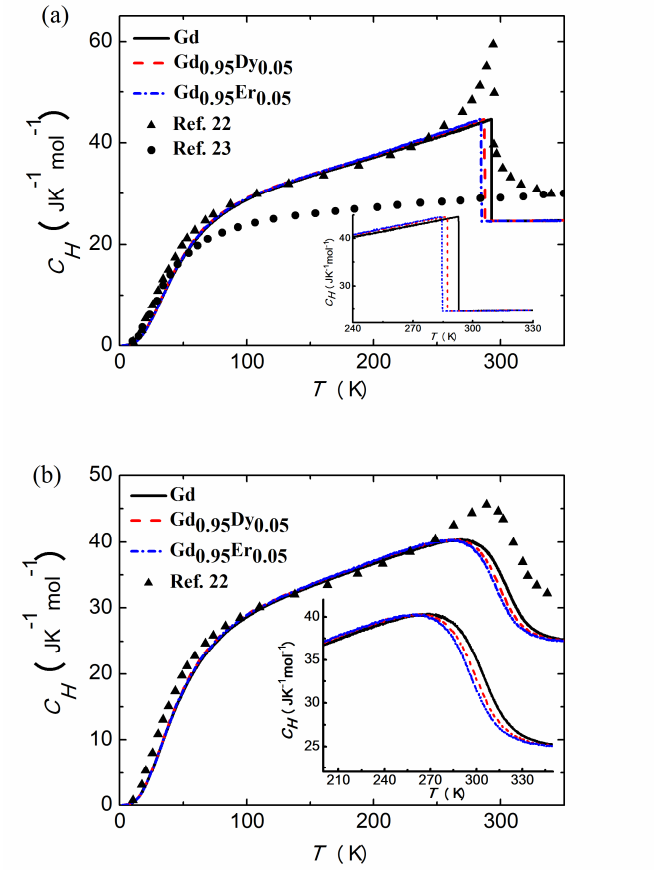

Fig. 2. The temperature dependency of heat capacities of Gd, $Gd_{0.95}Dy_{0.05}$ and $Gd_{0.95}Er_{0.05}$ (a) at the absence of applied magnetic field, and (b) under 2T applied magnetic field.

4.1.3 *The adiabatic temperature change of $Gd_{1-x}R_x$ in the magnetization or demagnetization process*

On the basis of Eq.(8), one can solve out numerically the adiabatic temperature change $(\Delta T)_{ad}$. Figure 3 shows the adiabatic temperature change $(\Delta T)_{ad}$ of Gd, $Gd_{0.95}Dy_{0.05}$ and $Gd_{0.95}Er_{0.05}$ versus temperature T curves with (a) magnetization or (b) demagnetization process. In the process of adiabatic demagnetization, the temperature of magnetic materials decreases. On the contrary, the temperature of the magnetic materials increases in the process of adiabatic magnetization. As shown in Fig.3, the adiabatic magnetization or demagnetization temperature change exhibits a caret-like shape curve for Gd, $Gd_{0.95}Dy_{0.05}$, and $Gd_{0.95}Er_{0.05}$ under 0-2T or 2-0T field variation. It is found from Fig.3 that the effect of magnetization or demagnetization on the adiabatic temperature change is weak, but the temperature dependence of the magnetization or demagnetization is distinct, at which the adiabatic magnetization temperature change of these materials attain its maximum value. For example, the maximum adiabatic temperature change of $Gd_{0.95}Dy_{0.05}$ is about 7.26 K either in the magnetization or demagnetization process, but the temperature at the maximum adiabatic temperature change of $Gd_{0.95}Dy_{0.05}$ in magnetization process is 287.5 K and the temperature at the maximum adiabatic temperature change of $Gd_{0.95}Dy_{0.05}$ in demagnetization process is 294.8 K.

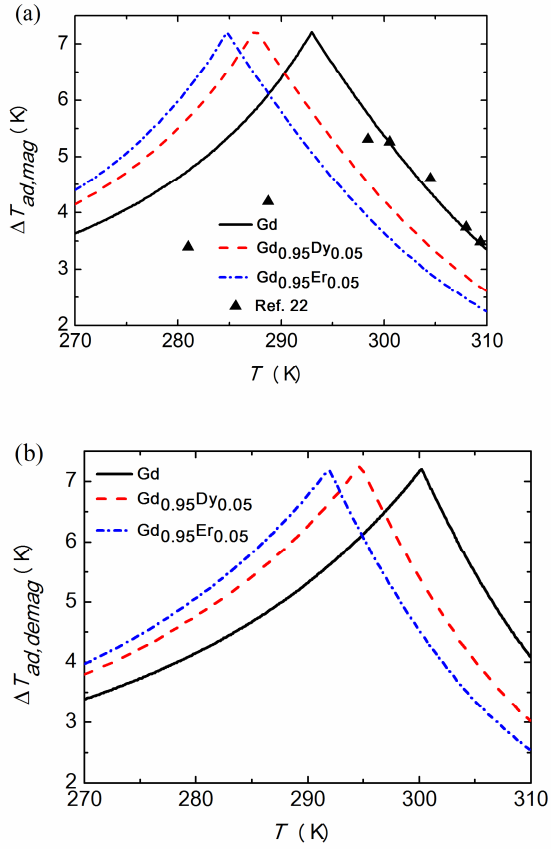

Fig. 3. The adiabatic magnetization/demagnetization temperature change of Gd, $Gd_{0.95}Dy_{0.05}$,and $Gd_{0.95}Er_{0.05}$

versus temperature curves under (a) 0-2T, and (b) 2-0T field change.

5. CONCLUSIONS

The magnetocaloric characteristics of Gd, $Gd_{1-x}Dy_x$, and $Gd_{1-x}Er_x$ are investigated numerically based on de Gennes model. It is found that the theoretical results for their Curie temperatures agree with the experimental ones. The Curie temperatures of Gd-R(R=Dy, Er) can be implemented by changing R-doped concentration *x*, and they decrease linearly as R-doped concentration increases. 0 T applied magnetic field gives rise to a sharp change of the heat capacity of Gd, $Gd_{0.95}Dy_{0.05}$, and $Gd_{0.95}Er_{0.05}$ when temperatures are close to their respective Curie temperatures. In these three materials, the heat capacity of $Gd_{0.95}Er_{0.05}$ is the largest when temperatures are approximately lower than 270K, and the heat capacity of Gd is the largest when temperatures are approximately higher than 270K. The changes of the adiabatic temperature change of Gd, $Gd_{0.95}Dy_{0.05}$, and $Gd_{0.95}Er_{0.05}$ are 0.003 K, 0.002 K, and 0.001K respectively from magnetization to demagnetization process. The maximum adiabatic temperature change of $Gd_{0.95}Dy_{0.05}$ is around 7.26 K that is largest among these three materials during the magnetization and demagnetization processes. The effect of the magnetization/demagnetization process on the temperatures at maximum adiabatic temperature change of Gd, $Gd_{0.95}Dy_{0.05}$, and $Gd_{0.95}Er_{0.05}$ is relatively obvious. The increased values of the temperatures at the maximum adiabatic temperature change of Gd, $Gd_{0.95}Dy_{0.05}$, and $Gd_{0.95}Er_{0.05}$ are 7.2K, 7.3K, and 7.1 K respectively from magnetization to demagnetization process. The results obtained in the present paper can provide some guidance for theoretical calculation of MCE materials and the parametric design of room-temperature magnetic refrigerators.

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