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New magnetic refrigeration materials for temperature range from 165 K to 235 K

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Abstract

In order to develop adequate rare earth refrigerants used below 250 K and avoid the negative magnetocaloric effect of Dysprosium and the expensive cost of Terbium, the heavy–light rare earth alloys are considered. In the present paper we report the magnetic entropy measurements for the alloys $(Gd,Dy)_{1-x}Nd_x$ (x=0, 0.1, 0.2, 0.3). These alloys, unlike most of the heavy rare earth metals, have only one magnetic ordering phase, that is, the ferromagnetic ordering.

Keywords: Rare earth; Magnetic refrigerant; Magnetic entropy change

1. Introduction

For the magnetic refrigeration in subroom temperatures, even though the manganese oxide perovskites with a large magnetic entropy change can be used as suitable refrigerants [1], the rare earth alloys should not be neglected, because these alloys are easily machined and have higher thermal conductivity [2]. Unfortunately, the first magnetic order phases (with decreasing temperature from the room temperature) in most of the heavy rare earth metals are antiferromagnetic. It results in a negative magnetocaloric effect (temperature rising when demagnetized) in the vicinity of the antiferromagnetic ordering temperature [3–5]. Thus it is difficult to use these metals together with other ferromagnetic refrigerants [6].

The introduction of light rare earths into heavy ones produces continuous solid solutions in a limited concentration range. Thus, only a few results of the neutron diffraction on this kind of alloys have been reported [7]. However, in recent years it is known that heavy–light rare earth alloys can be used as magnetic refrigerants and have some expected magnetocaloric properties. Addition of relatively small amounts of La (or Nd) to Er (or Dy) was observed to reduce the temperature range of complex magnetic ordering phases. In contract to the Dy–Y alloys, the Dy–Nd tends to stabilize the ferromagnetic-type structure with respected to the antiferromagnetic-type structure [2,7,8].

In order to develop the adequate rare earth refrigerants to be used below 250 K, in the present paper we report the investigation in magnetic entropy for the alloys $(Gd,Dy)_{1-x}Nd_x$ (x=0, 0.1, 0.2, 0.3). The Curie temperatures T_c of them are from 165 K to 235 K, and these alloys are of simple ferromagnetic ordering between 1.5 K and their respective T_c. As substitutional refrigerants the alloys have particular advantages to avoid the negative magnetocaloric effect of Dysprosium and the expensive cost of Terbium.

2. Experimental procedure

The purity quotients of all the starting metals used in preparation of the sample alloys were above 99.9%. The metals were alloyed together by arc melting in a water-cooled copper crucible under an argon atmosphere, and the produced button was turned over and remelted three times in order to ensure homogenization. The phase analysis was carried out by means of X-ray diffraction with CuKα. The samples used in magnetic measurements were of cylinder shape with 1.5 mm diameter and 6 mm length. The magnetic properties were measured using the extracting sample magnetometer. In order to reduce the influence of demagnetizing field in measurement processes the axes of

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the sample cylinders were kept parallel with the applied field.

The magnetization $M(T, H)$ measurements were carried out between 1.5 K and 300 K at applied magnetic fields up to 6.7 T. The magnetic entropy change was determined through a numerical integration,

$$\Delta S_M(T, H) = S_M(T, 0) - S_M(T, H) = -\mu_0 \int_0^H (\partial M/\partial T)_H \, dH \quad (1)$$

Before the integration, we had fitted the measured $M(T, H)$ with a customized Brillouin function to supply a lot of data points required by this integration.

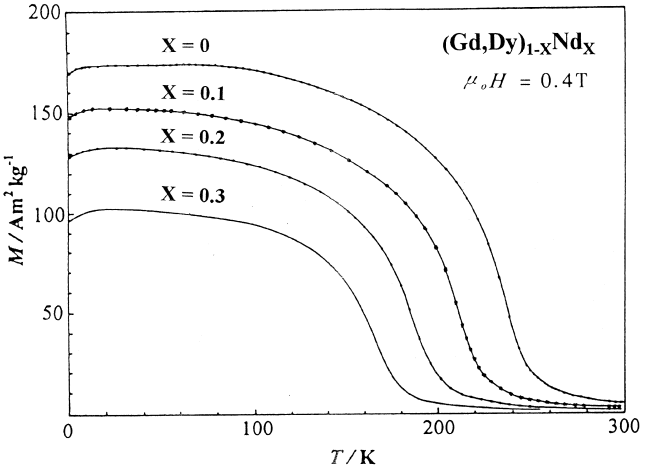

Fig. 1. Magnetization as a function of temperature ($\mu_0 H = 0.4$ for T) $x = 0$, 0.1, 0.2 and 0.3 samples. The measurements are carried out through ZFC processes, and the lines are guides to the eye.

3. Results and discussion

In the X-ray diffraction patterns of $(Gd,Dy)_{1-x}Nd_x$ ($x = 0$, 0.1, 0.2, 0.3) a regular change was observed. For $Gd_{0.5}Dy_{0.5}$, the pattern has a perfect characteristic of the hcp structure, the lattice parameters $a = 3.613$ Å and $c = 5.710$ Å. However, with increasing the Nd constituent x, the hcp(101) and (102) diffraction peaks become weaker and weaker, even though the intensity of the hcp(002) peak holds on. And for $Gd_{0.35}Dy_{0.35}Nd_{0.3}$, the hcp(102) along with other higher index peaks almost disappear. In general, this change reflects a deviation from perfect long-range order in the lattice (or a breakdown of the hexagonal symmetry in the basal plane of the hcp structure), which can causes a change of the magnetic ordering behavior. It is somewhat similar to the cases of the binary alloys, where the phase transition of $Dy_{0.7}Nd_{0.3}$ from paramagnetic to antiferromagnetic was smoothly going on instead of the sudden transition in the Dy–Y alloys [7].

In this paper, we let $M_0 = M$(1.5 K, 6.7 Tesla), which were measured by means of field cooling (FC), see Table 1. For $Gd_{0.35}Dy_{0.35}Nd_{0.3}$ $M_0 = 158.2$ Am^2/kg, which is only 59% that of the $Gd_{0.5}Dy_{0.5}$ sample. This means that the Nd ions seem to have no contribution to the total moment of $Gd_{0.35}Dy_{0.35}Nd_{0.3}$. The f electronic shells of Nd ions are markedly larger than that of Gd and Dy, therefore, the effect of crystal-field in heavy–light rare earth alloys is relatively more important than in heavy rare earth alloys. With increasing the Nd constituent in the alloys, the ratio of crystal-field splitting to exchange interaction increases. The crystal-field tends to destroy the orbital contribution to magnetic moments. In addition, because the spin–orbit coupling in Dy ions is also very strong, the orbital moment influenced by the crystal-field may hold back the spin moment from following the effect of an applied field. Thus, the total ionic moment is suppressed [9].

$M(T, 0.4$ Tesla) measured by zero field cooling (ZFC) processes are shown in Fig. 1, and the data are used to determine the ferromagnetic ordering temperature T_c of each sample, as shown in Table 1. It is well known that in order to calculate the magnetic entropy change, the magnetization in lower fields play a more important role, because $(\partial M/\partial T)_H$ in lower fields are usually larger than that in higher fields. Therefore, in following calculation we will be concerned about the $M(T,H)$ data fit in lower fields more than ever. In order to decide the reversibility of the magnetocaloric behavior, M(162 K, H) of $Gd_{0.35}Dy_{0.35}Nd_{0.3}$ were also measured. The result shows that for the field range from ±0.1 T to ±6 T the M(162 K, H) data points are positioned at the same smooth curves whenever the field increases or decreases. Besides, for $T = 162$ K, the residual magnetization $B_r < 3$ Am^2/kg and the coercive force $H_c = 150$ Oe. In general, this irreversibility can be neglected for the magnetic refrigeration application.

For the simple ferromagnetic materials (say Gd), the magnetization as a function of temperature and applied field can be described by the Brillouin function [10]. And for the simple crystal-field splitting materials (say $Gd_3Ga_5O_{12}$ when $T > 2$ K), the magnetization can also be fitted through a energy-level splitting model [11]. Unfortunately, so far there is no any satisfactory model to be

Table 1
Magnetic ordering temperature T_c and saturated magnetization M_0

	$Gd_{0.5}Dy_{0.5}$	$Gd_{0.45}Dy_{0.45}Nd_{0.1}$	$Gd_{0.4}Dy_{0.4}Nd_{0.2}$	$Gd_{0.35}Dy_{0.35}Nd_{0.3}$
M_0 (Am^2/kg)	270.1	235.2	200.9	158.2
T_c (K)	235	211	188	165

able to fit the magnetization in heavy–light rare earth alloys. It is because that the three effects, namely the Zeeman effect, the exchange interaction and the crystal-field effect, appear simultaneously in this kind of alloys. In order to obtain the magnetic entropy change of $(Gd,Dy)_{1-x}Nd_x$ by using Eq. (1), we have to first use a customized Brillouin function to fit the measured magnetization, that is,

$$M = M_0 B_J(x) \tag{2}$$

$$x = gJ\mu_B(H + \Delta H + \lambda M)/k_B T \tag{3}$$

$$M_0 = np = ngJ\mu_B = \alpha - \beta H^{-1/3} \tag{4}$$

$$\lambda = 3k_B T_c/\mu_0 ng^2 \mu_\beta^2 J(J+1) \tag{5}$$

where $B_J(x)$ is the Brillouin function, α and β are constants, $p = gJ\mu_B$ is the average ion effect moment, n is the number of magnetic ions per unit volume. The field dependence of M_0 is a feature of polycrystalline samples. With decreasing the field the g-factor will decrease, but λ increase. ΔH in Eq. (3) (for $x=0.3$, $\mu_0\ \Delta H=0.6$ T; for $x=0$, $\mu_0\ \Delta H=0.2$ T) is introduced in order to make compensation for the magnetization reduction (when $T > T_c$), which results from using Eq. (4). It should be emphasized that the fit of $(\partial M/\partial T)_H$ in the vicinity of T_c, which determines the maximum magnetic entropy change, is of the most important.

For $x=0.3$, the fitted $M(T, H)$ curves are shown in Fig. 2. As we see, below 130 K a good fit have not been realized, so that the calculated entropy change, shown in Fig. 3, is in force only in the limited temperature range from 130 to 200 K. For $Gd_{0.5}Dy_{0.5}$, the fitted magnetization curves along with the experimental data are shown in Fig. 4. By similar argument, the application of the calculated entropy change, shown in Fig. 5, should be limited in the temperature range from 200 to 270 K.

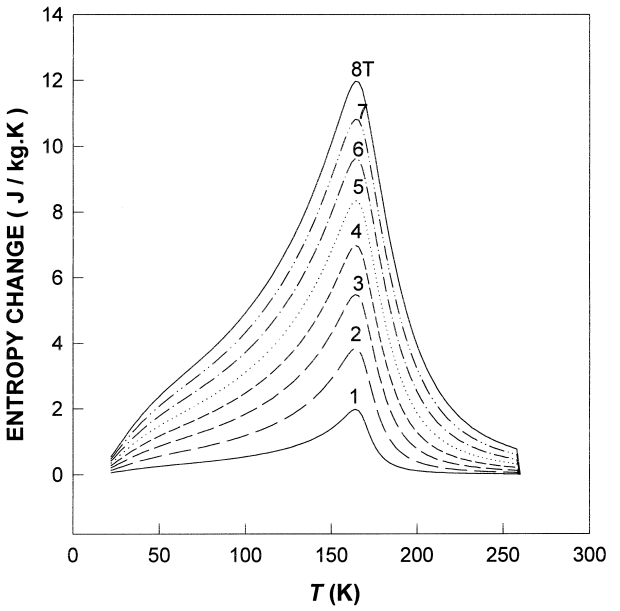

Fig. 3. Calculated magnetic entropy change as a function of temperature and applied fields for $x=0.3$ sample.

In a word, $(Gd,Dy)_{1-x}Nd_x$ as a kind of new magnetic refrigerants can be used in order to evade the negative magnetocaloric effects in Dy and Tb, also the expensive cost of Tb.

In order to identify the chronic effects in the samples, we measured these samples ones again after left in air for

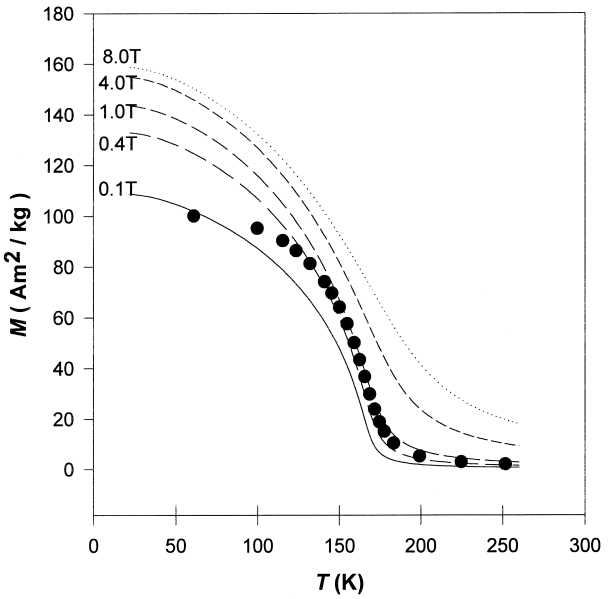

Fig. 2. Measured $M(T, 0.4$ Tesla) (solid circles) and calculated $M(T, H)$ (lines for various H) for $x=0.3$ sample.

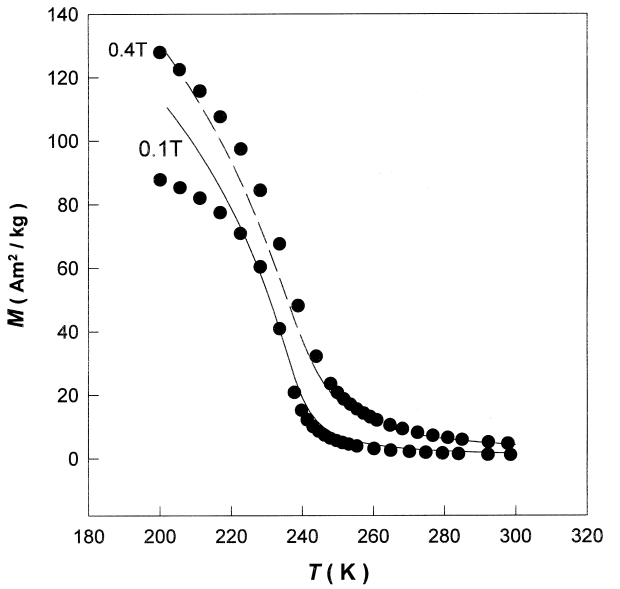

Fig. 4. Curves fitted according to the measured $M(T, 0.1$ Tesla) and $M(T, 0.4$ Tesla) (solid circles) for $Gd_{0.5}Dy_{0.5}$.

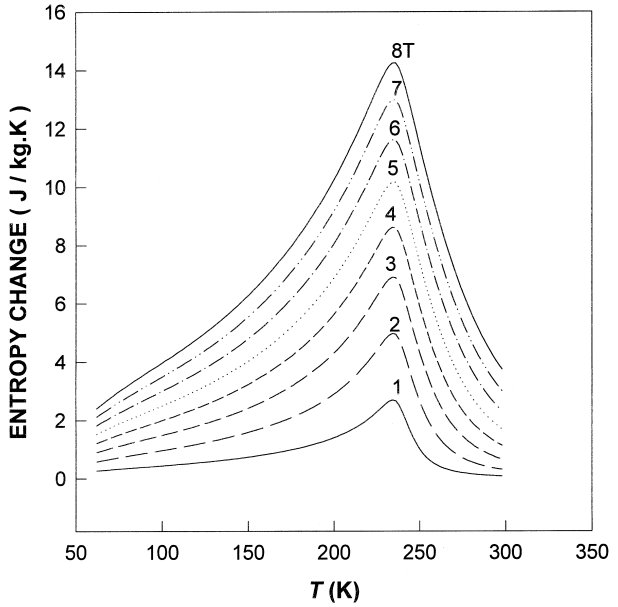

Fig. 5. Calculated magnetic entropy change as a function of temperature and applied fields for $Gd_{0.5}Dy_{0.5}$.

two years. The result shows that the samples did not appear to suffer subsequent oxidation, but did suffer crystalline grains growing up. For $Gd_{0.5}Dy_{0.5}$, the magnetization almost did not vary, while for $(Gd,Dy)_{1-x}Nd_x$ ($x \neq 0$), a large magnetization suppression was observed (~20% for $x = 0.3$ sample) after these samples were left in air for two years. The newly prepared polycrystalline Gd–Dy–Nd alloys have somewhat nanocrystalline characteristic, but as time goes on, the develop of crystalline grain sizes makes the Nd ion crystal-field effect become stronger and stronger, which results in the suppressed magnetization. This problem is worthy of note, when samples $(Gd,Dy)_{1-x}Nd_x$ ($x \neq 0$) as magnetic refrigerants are used.

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