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Thermomagnetic properties near transitions of Tb_6FeX_2 (X = Sb, Bi)

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Abstract

The thermomagnetic properties of compounds Tb_6FeX_2 (X = Sb, Bi) near the magnetic transition were investigated. The ferromagneticparamagnetic transition of the two compounds is a typical second-order transition. The Landau theory of second-order phase transition is employed to investigate the thermodynamic transition temperature and the specific heat. The magnetic entropy change was also calculated. The specific heat jumps of the compounds Tb_6FeSb_2 and Tb_6FeBi_2 at Curie point are 36.5 and 41.2 J kg⁻¹ K⁻¹, respectively. The maximum magnetic entropy change of the compound Tb_6FeBi_2 is 2.68 J kg⁻¹ K⁻¹ occurring around 246 K, while the maximum magnetic entropy change of Tb_6FeSb_2 is 2.25 J kg⁻¹ K⁻¹ at 256 K.

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1. Introduction

Magnetic refrigerant materials based on the magneto-caloric effect have attracted much attention since studies on rare-earth based compounds have revealed a large effect near room temperature. Compared with gas refrigerators, magnetic refrigerators have a number of advantages such as high efficiency, energy saving and environmental concerns. It has been shown that heavy-rare-earth elements and their compounds are the promising potential materials for finding a large magneto-caloric effect due to their high magnetic moments. In our previous work [1], our group has studied the structure and magnetic properties of a new compound Tb₆FeSb₂ with a Curie temperature of 256 K. Morozkin et al. [2] also reported the isostructural compound Tb₆FeBi₂with the Curie temperature at 250(5) K. The sharp changes in magnetization of two compounds at T_c motivated us to study the magnetic behaviors and thermomagnetic properties which allow the estimation of the magneto-caloric effects in this system. Here, we presented the results.

2. Experimental

The sample Tb₆FeSb₂ prepared in our previous work [1] was adopted. A total of five Tb₆FeBi₂ samples were prepared by arc-melting of pure metal pieces (99.9%Fe, 99.9%Tb and 99.99%Bi) under high pure argon atmosphere. To ensure the homogeneity of the samples, they were melted three times. In order to compensate the losses of Bi in the process of melting, an extra amount of 0.4%Bi, 0.6%Bi, 0.8%Bi, 1.0%Bi and 1.2%Bi was added into the five samples, respectively. Furthermore, each sample was melted under an electric current as low as possible to minimize the weight losses of Bi. After melting, all samples were enclosed in an evacuated quartz tube and annealed at 1073 K for 600 h, and the alloys were then cooled down to 773 K at a rate of 10 K/h and kept for 240 h. Finally, all samples were quenched into liquid nitrogen. All the alloys were analyzed by the X-rays diffraction method. The alloy with the single phase was selected for further analysis. The Rietveld method was also employed to check structure of the Tb₆FeBi₂. Magnetic measurements for the compounds Tb₆FeSb₂ and Tb₆FeBi₂ were performed by a vibrating sample magnetometer (VSM, Lake Shore 7410).

3. Results and discussion

3.1. Structures

The Rietveld refinement of Tb₆FeBi₂ was performed by using the DBWS9411 program. The observed and calculated data and residuals of the X-ray powder diffraction patterns of Tb₆FeBi₂ are shown in Fig. 1. The refined lattice parameters are a=0.83128(3) nm, and c=0.41957(2) nm, space group $P\bar{6}2m$

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Fig. 1. The observed and calculated data and residuals of the powder diffraction patterns of Tb_6FeBi_2 .

(No. 189). The result agrees well with that of the literature [2]. The lattice parameters of two compounds Tb_6FeSb_2 and Tb_6FeBi_2 are given in Table 1.

3.2. Magnetic behaviors

Temperature scans of the magnetization under an applied DC magnetic field of 0.1 T point out that the Curie temperature of Tb₆FeBi₂ is 246 K, which is in agreement with the reported value in Ref. [2]. The Curie temperature of Tb₆FeSb₂is 256 K. Figs. 2(a) and 3(a) show the isothermal magnetization versus magnetic field curves, i.e., M-H curves at various temperatures for the compounds Tb₆FeSb₂ and Tb₆FeBi₂. Figs. 2(b) and 3(b) are the enlargements of the typical magnetization curves of the two compounds Tb₆FeSb₂ and Tb₆FeBi₂ measured in increasing and decreasing fields below or near their Curie temperatures. It can be seen that both compounds exhibit reversible behaviors between the increasing and decreasing fields. No hysteresis means that both samples show soft magnetic behavior in the temperature range.

Fig. 4 gives the Arrott curves near the magnetic transitions of the two compounds Tb_6FeSb_2 and Tb_6FeBi_2 . These curves display good linear fits for all the dots except several points in the low-field regions. It is evident that both of the ferromagnetic–paramagnetic transitions of the two compounds are second-order transition.

3.3. Specific heat

Table 1

Near the transition, the Landau theory of second-order phase transition predicts the following relationship [3,4]:



Fig. 2. (a and b) Isothermal magnetization M vs. magnetic field H curves at various temperatures of compound Tb₆FeSb₂.

$$\alpha + \beta M^2 = \frac{H}{M},\tag{1}$$

According to this equation, the measured M-H curves of the two compounds were then transformed into H/M versus M^2 curves, seen in Fig. 5. No demagnetization correction was applied for two reasons:

- (1) the irregular shape of samples did not facilitate an error free correction;
- (2) for non-collinear alloys, the M values are low enough to make any demagnetization corrections negligible.

From Fig. 5, it can be seen that the $H/M-M^2$ curves of the two compounds are linear in the regions of true magnetization when

Structural and thermomagnetic parameters of compounds Tb_6FeSb_2 and Tb_6FeBi_2

Compounds	Lattice parameters		<i>T</i> _c (K)	$\Theta(\mathbf{K})$	$\Delta S_{\rm M}^{({\rm max})} ({\rm Jkg^{-1}K^{-1}})$	$T(\mathbf{K})$ at $\Delta S_{\mathbf{M}}^{(\max)}$	$\Delta C_{\rm P} (\mathrm{Jkg^{-1}K^{-1}})$
	a (nm)	<i>c</i> (nm)					
Tb ₆ FeSb ₂	0.81942(5)	0.41758(3)	256	252	2.24	256	36.5
Tb ₆ FeBi ₂	0.83128(3)	0.41957(2)	246	244	2.67	246	41.2

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