

Magnetocaloric Effect of the $\text{Tb}_{1-x}\text{Y}_x\text{NiAl}$ and $\text{TbNiAl}_{1-y}\text{In}_y$ Series

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We have studied the development of the magnetocaloric effect in the $(\text{Tb},\text{Y})\text{NiAl}$ and $\text{TbNi}(\text{Al},\text{In})$ series as determined from magnetization measurements. The transition from antiferromagnetic order in TbNiAl to ferromagnetic order in $\text{Tb}_{0.7}\text{Y}_{0.3}\text{NiAl}$ is accompanied by increase of the maximum entropy change from -4.1 to $-4.4 \text{ J kg}^{-1} \text{ K}^{-1}$. In the $\text{TbNi}(\text{Al},\text{In})$ series, the change of uniaxial anisotropy in TbNiAl to the easy-plane anisotropy in TbNiIn leads to broadening of the magnetocaloric effect accompanied with large increase of the relative cooling power from 66 to 120 J kg^{-1} .

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1. Introduction

The magnetocaloric effect (MCE) is characterized by the adiabatic temperature or isothermal entropy change of the sample when the magnetic field is changed. This is due to the fact that the entropy of a crystalline solid depends highly on the lattice vibrations and also on order/disorder of the magnetic moments. The magnetocaloric refrigeration attracts great attention as a promising replacement for the conventional gas compression method. It is of high interest to study magnetocaloric materials which are useful for refrigeration in a wide temperature region. The substituted materials are often studied to tune the magnetocaloric properties. The substitutions affect the microscopic interactions within the material, and hence can lead to a change of the transition temperatures, maximum entropy change and of the whole character of MCE.

In this work, we investigate how the MCE is influenced by a change of the type of magnetic order and change of the magnetocrystalline anisotropy in two isostructural series of compounds: $(\text{Tb},\text{Y})\text{NiAl}$ and $\text{TbNi}(\text{Al},\text{In})$, all crystallizing in the hexagonal ZrNiAl -type structure. TbNiAl orders antiferromagnetically below $T_N = 45 \text{ K}$ with Tb moments aligned along the c -axis and $1/3$ of Tb moments strongly reduced in magnitude [1, 2]. Transition to another antiferromagnetic phase with equal moment size, keeping the easy-axis anisotropy, takes place at $T_1 = 23 \text{ K}$. Metamagnetic transition to ferromagnetic state occurs when magnetic field of $\approx 0.5 \text{ T}$ is applied along the c -axis [1, 2]. The Y substitution in the $\text{Tb}_{1-x}\text{Y}_x\text{NiAl}$ series leads to decrease of the transition

temperature and gradual transition from the antiferromagnetic to ferromagnetic ordering which is well established for $x \geq 0.1$ [2]. The magnetocrystalline anisotropy remains unchanged with Y substitution. On the other hand, the change from the easy-axis to the easy-plane anisotropy occurs in $\text{TbNi}(\text{Al},\text{In})$ compounds. TbNiIn orders magnetically around 70 K and undergoes further magnetic phase transition at 26 K . Complex non-collinear arrangement of Tb moments within the basal plane was reported for TbNiIn [3, 4].

2. Experimental

The $\text{Tb}_{1-x}\text{Y}_x\text{NiAl}$ ($x = 0.03, 0.06$ and 0.30) and $\text{TbNiAl}_{1-y}\text{In}_y$ ($y = 0.2, 0.4, 0.7$ and 1.0) samples were prepared by melting of pure elements in a monoarc furnace under an argon atmosphere. The ingots were remelted several times to ensure the homogeneity. Crystal structure was verified by powder X-ray diffraction and the composition was confirmed by energy dispersive X-ray (EDX) analysis. The magnetization measurements were performed on the PPMS instrument (Quantum Design) using powder samples consisting of randomly oriented grains fixed by a nonmagnetic glue. The magnetization isotherms up to 2 T were measured in a wide temperature range with step of 2 or 4 K . The entropy change, ΔS was then calculated using the equation derived from the Maxwell relation. The final approximate equation as well as detailed discussion of the combined error of such indirect measurement of the isothermal entropy change was done by Pecharsky et al. [5]. The error of the entropy change calculated from our data can be estimated to about 15% in the vicinity of the maximum of ΔS .

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3. Results

The magnetic ordering temperatures, T_{ord} , as inferred from the $M(T)$ dependences are summarized in Table. The transition temperatures are generally in agreement with previously published values [2, 3]. The determined entropy change for the $Tb_{1-x}Y_xNiAl$ compounds is shown in Fig. 1. The entropy change of the pure $TbNiAl$ is lower than the previously reported data [6]. This difference will be discussed in detail in a forthcoming paper together with the single-crystal data. Some texture in the sample used in Ref. [6] could be possible reason. The temperature dependence of the entropy change for samples with low content of Y ($\leq 6\%$) has qualitatively the same shape as for $TbNiAl$. The anomalies related to the magnetic phase transitions at T_{ord} and T_1 shift slightly to lower temperatures. The low-temperature transition is not visible for $Tb_{0.7}Y_{0.3}NiAl$ which is in agreement with the expected pure ferromagnetic state in this compound [2]. The entropy change for field change of 2 T takes the maximum of $\Delta S_{max} = -4.4 \text{ J kg}^{-1} \text{ K}^{-1}$ in $Tb_{0.7}Y_{0.3}NiAl$ at temperature of $T_{max} = 39 \text{ K}$. It is remarkable that the replacement of one third of Tb atoms with nonmagnetic Y leads to the increase of the magnetocaloric effect, especially the relative cooling power (RCP) which is defined as a product of the maximum entropy change and full width at half maximum of the $\Delta S(T)$ peak. This interesting behavior is related to microscopic change of the magnetic structure from antiferromagnetic to ferromagnetic. The MCE characteristics for the Y substitution are summarized in Table.

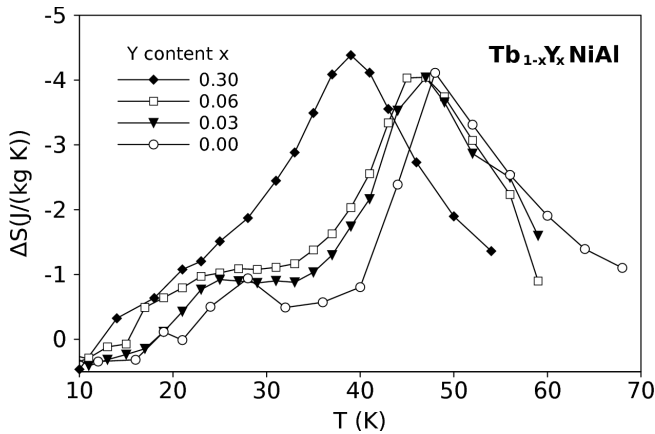


Fig. 1. The entropy change for the $Tb_{1-x}Y_xNiAl$ series determined for the field change of 2 T.

In the $TbNi(Al,In)$ series, the transition temperatures first slightly decrease with increasing In content to the minimum of 39 K in $TbNiAl_{0.5}In_{0.5}$ and then increase to 70 K in pure $TbNiIn$. These results suggest that the In substitution first suppresses the antiferromagnetic ordering with uniaxial anisotropy, the easy-plane magnetic order develops in compounds with $\approx 50\%$ of In and further addition of In stabilizes this magnetic structure and

TABLE

The ordering temperature T_{ord} , the temperature T_{max} at which the maximum entropy change ΔS_{max} was obtained for the field change of 2 T, the full width at half maximum δT_{FWHM} of the $\Delta S(T)$ peak and the relative cooling power in the studied compounds.

x/y	T_{ord} [K]	T_{max} [K]	ΔS_{max} [J/(kg K)]	δT_{FWHM} [K]	RCP [J/kg]
$Tb_{1-x}Y_xNiAl$					
0.00	47	48	-4.1	16	66
0.03	46	47	-4.0	17	68
0.06	45	47	-4.0	17	68
0.30	41	39	-4.4	18	79
$TbNiAl_{1-y}In_y$					
0.0	47	48	-4.1	16	66
0.2	46	48	-3.1	24	74
0.5	42	39	-4.7	20	94
0.7	47	45	-4.1	26	107
1.0	72	53	-2.4	50	120

the ordering temperature increases. The calculated entropy change for all samples is shown in Fig. 2 and the magnetocaloric characteristics are given in Table. The

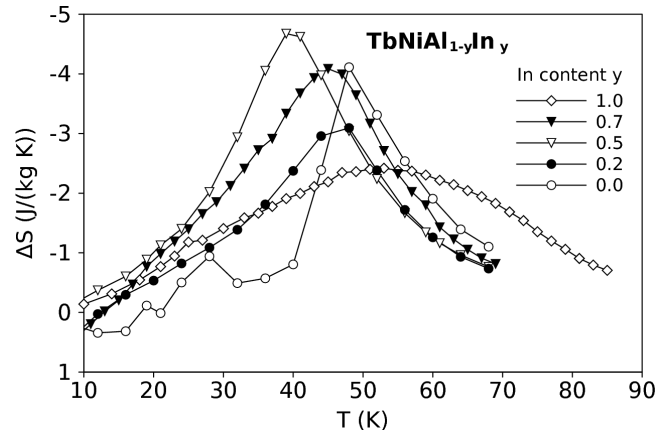


Fig. 2. The entropy change for the $TbNiAl_{1-y}In_y$ series determined for the field change of 2 T.

low-temperature anomaly is absent already for 20% of In. The main observed feature is the increasing broadening of the ΔS anomaly at temperatures below T_{ord} . This behavior leads to a large increase of the RCP value from 66 J kg^{-1} for $TbNiAl$ to 120 J kg^{-1} for $TbNiIn$, although $TbNiIn$ exhibits much lower values of the maximum entropy change (see Fig. 2 and Table).

4. Conclusions

The temperature width of MCE, and hence also the RCP value, in the studied $(Tb,Y)NiAl$ and $TbNi(Al,In)$

series is increasing with increasing Y or In content. This is presumably related to the change from antiferro- to ferromagnetic ground state in (Tb,Y)NiAl compounds and to the change of the magnetocrystalline anisotropy in TbNi(Al,In) compounds. The neutron diffraction data are desirable to reveal microscopic details responsible for the behavior of TbNi(Al,In) compounds.

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