Large inverse magnetocaloric effect in single crystal TbNiAl$_4$

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Abstract. The magnetocaloric effect (MCE) in a TbNiAl$_4$ single crystal was firstly investigated by magnetization and heat capacity measurements. Along a-axis the sample exhibits a large inverse MCE, where the material cools when a field is applied. The maximum value of magnetic entropy change ($\Delta S_M^{\text{max}}$) and adiabatic temperature change ($\Delta T_{ad}^{\text{max}}$), for a field change of 4 T and at around 20 K, are found to be 5.1 J/Kg K and -3.3 K, respectively. It is proposed that the large inverse entropy change is associated with the sensitive field dependent magnetic phase transition.

1. Introduction

In the last two decades, magnetic materials with a large magnetocaloric effect (MCE) have been studied extensively, both experimentally and theoretically, since there is great interest in the application for magnetic refrigeration [1, 2]. The MCE manifests as the isothermal magnetic entropy change or the adiabatic temperature change of a magnetic material when it is exposed to a varying magnetic field. The magnetic refrigeration based on MCE is advantageous being an environment friendly and energy efficient refrigeration mechanism, which is expected to be a dominant future cooling technology [1-3]. A large value of MCE is considered to be the most important requirement for the application, and therefore it is strongly desirable to find new materials with large MCEs especially at low magnetic fields and with a wide temperature range. Most of the magnetocalorics exhibit a positive MCE associated with a Curie transition. Only a few materials like FeRh [4], Ni$_{50}$Mn$_{50-x}$M$_x$ (M = In and Sn etc.) [5] and CoMnSi$_{1-x}$Ge$_x$ [6] are known to exhibit an inverse magnetocaloric effect, where the material cools when a field is applied.

The ternary intermetallic compounds, RNiAl$_4$ (R=Y, rare earth) which crystallize in YNiAl$_4$-type orthorhombic structure have attracted some attention due to interesting magnetic properties [7-9]. Recently, Hutchison et al., [8] studied the magnetic properties of TbNiAl$_4$ single crystals by magnetization measurements and neutron diffraction, and two obvious magnetic phase transitions were observed. Interestingly, no studies of the magnetocaloric effect (MCE) in RNiAl$_4$ systems have been reported. In this paper the MCE in a TbNiAl$_4$ single crystal was studied. It is found that along the a-axis, the sample exhibits a large inverse MCE. The temperature dependence of the magnetic entropy change ($\Delta S_M$) and adiabatic temperature change ($\Delta T_{ad}$) were reported.
2. Experimental
The single crystal of TbNiAl₄ used in this work was grown by the Czochralski pulling method. The
crystallographic orientation was determined by the Laue X-ray back reflection method. The
magnetization measurements were done using a superconducting quantum interference device
magnetometer (Quantum Design, MPMS-7) in the temperature range 2 to 290 K, and DC magnetic
fields from 0 to 4 T. The specific heat measurements were carried out by the adiabatic heat relaxation
method, in the temperature range 2 to 40 K, using a Quantum Design physical property measurement
system (PPMS-9).

3. Results and discussion
The temperature dependence of magnetization along the a-axis at 1 T for TbNiAl₄ (2 to 290 K) is
shown in Fig. 1. Two phase transitions can be seen around 35 K (Tₘ₁) and 27K (Tₘ₂), which were
consistent to previous reported results [8]. The inset of Fig. 1 shows the temperature dependence of
magnetization along a-axis at 2, 3 and 4 T from 2 to 60 K. Note that Tₘ₁ was almost unchanged, but in
contrast, Tₘ₂ clearly shifts to lower temperature with increasing field. This field sensitive magnetic
phase transition behavior generally results in a large magnetocaloric effect.

![Figure 1](image.png)

**Figure 1.** Temperature dependence of magnetization for TbNiAl₄ at
1 T magnetic field. The inset shows the temperature dependence of
magnetization at 2, 3 and 4T.

In order to explore the magnetocaloric properties of TbNiAl₄, the magnetization isotherms of
TbNiAl₄ were measured at selected temperatures from 5 to 30 K and to maximum applied fields of 4 T
along the a-axis. The magnetic entropy change ∆Sₘ was calculated based on the results of the
magnetization isotherms using the integrated Maxwell relation [10]:

\[
\Delta S_M(T, \Delta H) = \int_0^\mu \left( \frac{\partial M(H, T)}{\partial T} \right)_H dH \approx \frac{1}{\delta T} \left[ \int_0^\mu M(T + \delta T, H) dH - \int_0^\mu M(T, H) dH \right].
\]  

(1)
Figure 2. The temperature dependence of magnetic entropy change $\Delta S_M$ under 4 T for TbNiAl$_4$ single crystal.

The $\Delta S_M$ was calculated using this technique for TbNiAl$_4$ from 5 to 30 K with 4 T applied along a -axis and is shown in Fig. 2. $\Delta S_M$ is positive, which means that the entropy increased when a field is applied (below 30 K). The $\Delta S_M$ data, with a field change of 4 T, has a broad peak from 18 to 28 K with value of at least 4.5 J/Kg K across nearly this whole range.

Figure 3. The temperature dependence of adiabatic temperature change $\Delta T_{ad}$ under 4 T for TbNiAl$_4$ single crystal. The inset shows the temperature dependence of specific heat $C$ in zero field.
Another important parameter for a MCE material is the adiabatic temperature change $\Delta T_{ad}$. The $\Delta T_{ad}$ can be roughly estimated using the approximation of [10]:

$$\Delta T_{ad} = T[S_M, H \neq 0(T) - S_M, H=0(T)]/C(T) \tag{2}$$

The inset of Fig. 3 shows the temperature dependence of specific heat ($C$) of TbNiAl$_4$ at zero field. Two obvious peaks were observed at 27 and 35 K, consistent with the magnetization results. The temperature dependences of $\Delta T_{ad}$ calculated using the equation (2), for TbNiAl$_4$ from 10 to 40 K and with 4 T along a-axis is shown in Fig. 3. The value of $\Delta T_{ad}$ has a large peak with a maximum value of -3.3 K at ~20 K for a field change of 4T. The origin of such a large inverse MCE in TbNiAl$_4$ is likely the sensitive field dependence of the magnetic phase transition at $T_{M2}$. Further more detailed studies of the MCE in this and related compounds are planned.

4. Conclusions

In summary, the magnetic properties, magnetic entropy change ($\Delta S_M$) and adiabatic temperature change ($\Delta T_{ad}$) were studied for a TbNiAl$_4$ single crystal. Two obvious magnetic phase transitions were confirmed around 35 K ($T_{M1}$) and 27K ($T_{M2}$) via the temperature dependence of magnetization and heat capacity. A large inverse MCE were observed along the a-axis. The maximum value of $\Delta S_M$ and maximum value of $\Delta T_{ad}$ for a field change of 4 T are around 5.1 J/Kg K and -3.3 K around 20 K, respectively.

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