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Magnetocaloric effect in terbium diboride

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ABSTRACT

Magnetocaloric effect has been investigated in TbB_2 in the vicinity of a second-order magnetic transition at 144 K. The maximum magnetic entropy change $-\Delta S_M$ is 12.7 J kg^{-1} K^{-1} for a field change from 0 to 7 T. The relative cooling power and adiabatic temperature change ΔT_{ad} are 256 J kg^{-1} T^{-1} and 29.5 K for a field change from 0 to 5 T. For a low-field change from 0 to 2 T, considerable $-\Delta S_M$ (5.2 J kg^{-1} K^{-1}) and ΔT_{ad} (14.7 K) are obtained with a cooling power of 67.6 J kg^{-1} T^{-1}, suggesting TbB_2 a good candidate for magnetic refrigerant around 144 K.

1. Introduction

Magnetocaloric effect (MCE) has come out as an attracting cryogenic technology because of its energy-efficient and environmental-friendly solid-state working substance [1]. According to the theory for MCE, magnetic materials with large effective moment (μ_{eff}) per atom and sharp slopes in their M–T curves are desirable for magnetic-induced cooling. The MCE of rare earth (RE) metals and compounds are therefore substantially investigated, due to their excellent magnetic properties [2–5]. On the other hand, a wide diversity of structural, physical, and physicochemical properties (such as high hardness, metallic conductivity, and a complex nature of magnetic ordering) has been found in RE borides [6]. It will also be of particular interest to study the MCE of the RE borides. Usually, in applications of magnetocaloric materials, there are some pitfalls in the first-order magnetic transition, such as slow kinetic responses, and noticeable thermal/magnetic hysteresis [7]. It is disputable for very large values reported for isothermal magnetic entropy change ($-\Delta S_M$) in some colossal MCE materials, which are based on the first-order magnetic transition [8]. The pursuit of highly efficient and reversible MCE compounds with a second-order magnetic transition has become a more attractive issue, practically, for application. Will et al. reported that ferromagnetic TbB_2 has an effective moment of 8.3 μ_B/Tb^{3+}, with its Curie temperature T_C of 151 K [9]. A large enthalpy change in TbB_2 at about 143 K by specific heat measurements [6] may foresee that TbB_2 has a remarkable $-\Delta S_M$ near to its T_C. In this work, we synthesized TbB_2 block by arc melting and report on a large reversible magnetic entropy change and a high relative cooling power in the vicinity of a second-order magnetic transition in TbB_2.

2. Experimental

The TbB_2 compound was prepared by arc melting 99.9 wt% Tb and 99.99 wt% B with an Tb:B atomic ratio of 1:2. X-ray diffraction (XRD) data of the TbB_2 compound were recorded by a D/max 2500PC diffractometer with Cu K_α radiation at 50 kV and 300 mA. It was indexed to be AlB_2-typed TbB_2 with a space group of $P6/mmm$, and very weak Tb peaks can be found in the XRD pattern as shown in Fig. 1. Magnetic measurements were carried out using a superconducting quantum interference device (SQUID, Quantum Design MPMS-7).

3. Results and discussion

Fig. 2 shows the temperature dependence of zero-field-cooling (ZFC) and field-cooling (FC) magnetization (M) of TbB_2 compound measured under a magnetic field of 0.01 T. A typical ferromagnetic–paramagnetic transition can be seen in Fig. 2. T_C of TbB_2 is determined to be about 144 K by the minimum of the differential of M–T curve shown as the inset of Fig. 2, which is in good agreement with the result of specific heat measurement [6], but a little lower than the Will et al.'s result [9]. A significant thermal irreversibility between ZFC and FC curves is observed below T_C, which may be attributed to the domain-wall pinning effect [13].

As shown in Fig. 3, isothermal M–H curves were recorded between 130 and 166 K with a temperature step of 4 K. The magnetization rapidly increases in a weak field region at low temperatures and shows a tendency to saturate with increasing field, indicating a typical behavior of ferromagnetic materials. A good coincidence between increasing- (solid square lines) and decreasing-field (solid circle lines) curves in the vicinity of T_C shows the absence of magnetic hysteresis. This is a good sign of magnetic reversibility for potential application in magnetic cooling. Fig. 4 shows Arrott plots

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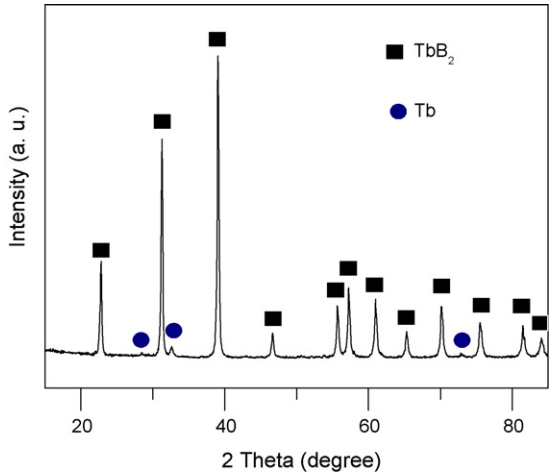

Fig. 1. XRD pattern for TbB_2 compound recorded at room temperature.

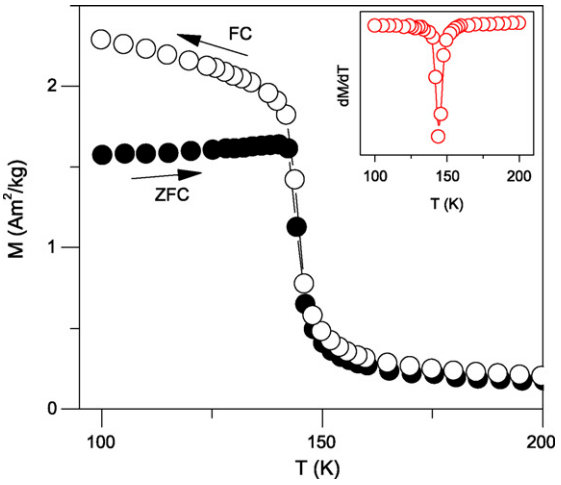

Fig. 2. Temperature dependences of ZFC and FC magnetization for TbB_2 compound under a magnetic field of 0.01 T. Inset is the differential of field-cooling M–T curve.

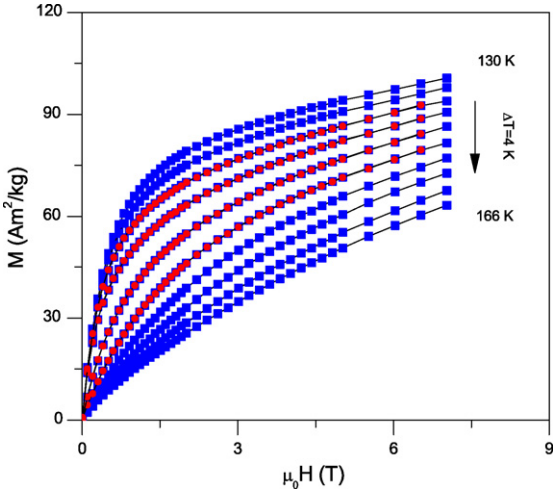

Fig. 3. Isothermal M–H curves for TbB_2 between 130 and 166 K with a temperature step of 4 K. Solid square lines and solid circle lines denote the increasing- and decreasing-field magnetization curves, respectively.

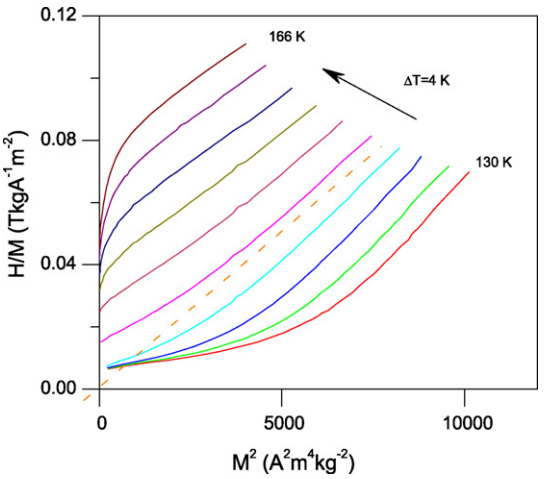

Fig. 4. Arrott plots of TbB_2 derived by the M–H curves in Fig. 3. Dashed line is extrapolated from the high-field part at the Curie temperature of 144 K.

(H/M versus M^2), which has been extensively used to distinguish the magnetic ordering of materials [14]. As described by the Landau expansion theory, the magnetic free energy near T_C can be expanded in powers of magnetization M neglecting higher order parts as:

$$F(M, T) = AM^2 + BM^4 - MH + \ldots \quad (1)$$

Here A and B are temperature-dependent parameters, called Landau coefficients. According to the Banerjee criterion [15,16], a magnetic transition is expected to be of the first order when the slope of H/M versus M^2 plot is negative (i.e. $B < 0$), whereas it will be of the second order when the slope is positive (i.e. $B > 0$). It is very clear that the Arrott plot for TbB_2 shows a characteristic second-order magnetic transition in the complete M^2 range.

According to the equilibrium condition $\partial F(M, T)/\partial M = 0$ of Eq. (1), one can obtain:

$$\frac{H}{M} = 2A + 4BM^2 \quad (2)$$

When $T = T_C$, the extrapolated intersection of the high-field H/M versus M^2 curve with the H/M axis is, by definition, zero. This zero-intersection is well produced by extrapolating the high-field part of the Arrott plot of TbB_2 at the Curie temperature of 144 K (see the dashed line in Fig. 4). A noticeable deviation from linearity near T_C is observed in the low-field range of the Arrott plot, which may be caused by a very small amount of terbium impurity. It should be mentioned that, apart from the itinerant-electron systems, the Arrott plots are in principle meant to be applied only to low-field magnetization data where the relative magnetization is much smaller than unity. However, the Arrott plots often also appear to be very sensitive for magnetic impurities, secondary phases, etc. Although the question may arise whether the relative magnetization is still much smaller than unity, it is better to neglect the data at the lowest fields. In the present case this seems true.

The magnetic entropy change $-\Delta S_M$ of TbB_2 is calculated from isothermal magnetization curves by using the Maxwell relation. It is believed that Tb impurity has insignificant influence on the total magnetic entropy change of the present TbB_2 sample mainly because of two reasons: (1) the amount of Tb is very small in the present sample; (2) the corresponding temperature (144 K) of the maximum $-\Delta S_M$ in TbB_2 is far lower than the ferromagnetic–antiferromagnetic transition at about 220 K of Tb [17]. The values of $-\Delta S_M$ as a function of temperature for different magnetic field changes are shown in Fig. 5. The temperature dependence of $-\Delta S_M$ shows a maximum value at about 144 K,

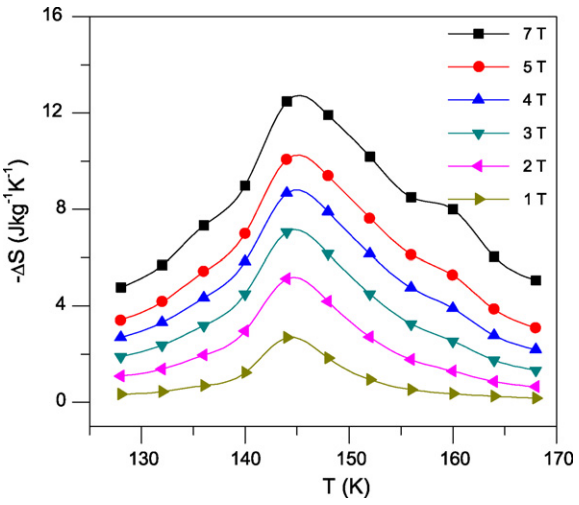

Fig. 5. Magnetic entropy change as a function of temperature for TbB_2 at different magnetic field changes.

which increases monotonically with the applied magnetic field and reaches 10.3 and 12.7 J kg^{-1} K^{-1} for a magnetic field change from 0 to 5 T and from 0 to 7 T, respectively. The maximum entropy changes $-\Delta S_M$ for a low-field change from 0 to 1 T and from 0 to 2 T are 2.7 and 5.2 J kg^{-1} K^{-1}, respectively. This magnetic entropy change is much higher than those reported in the same temperature range (between 70 K and room temperature) [10–12].

The relative cooling power $-\Delta S_{\max}\ {}_M\delta T_{fwhm}$ is a measure of how much heat energy can be transferred between cold and hot sinks in an ideal refrigerant cycle, which is of practical significance [18,19]. Here δT_{fwhm} is the full width at half maximum $-\Delta S_M$, namely, temperature difference at half values of the magnetic entropy change peak. The cooling power of TbB_2 is calculated to be 67.6 and 256 J kg^{-1} T^{-1} for a magnetic field change from 0 to 2 T and from 0 to 5 T, respectively. To further investigate the application potential of this compound, we consider the adiabatic temperature change $\Delta T_{ad} = -\Delta S_M(T_0, H) \times T_0/C_p(T_0, H_0)$, where $C_p(T_0, H_0)$ is the zero-field specific heat, as reported in Ref. [6]. The maximum values of ΔT_{ad} are estimated to be 14.7 and 29.5 K, respectively, for a magnetic field change from 0 to 2 T and from 0 to 5 T. All the above results reveal the terbium diboride as an interesting magnetic cooling material.

4. Conclusion

In summary, magnetocaloric effect has been investigated in terbium diboride in the vicinity of a second-order magnetic transition at 144 K. The maximum values of magnetic entropy change $-\Delta S_M$ and adiabatic temperature change ΔT_{ad} are 12.7 J kg^{-1} K^{-1} and 29.5 K, respectively, corresponding to the magnetic field change from 0 to 7 T and from 0 to 5 T. Relative cooling power of TbB_2 is found to be 256 J kg^{-1} T^{-1} for a field change from 0 to 5 T. The large reversible magnetic entropy change and high cooling power make TbB_2 to be a promising cooling material applicable in a temperature region around 144 K.

Acknowledgements

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