Magnetocaloric properties of single crystalline YbTiO₃ with second order phase transition

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Abstract. Magnetic entropy change and refrigerant capacity in applied magnetic fields up to 5 T have been investigated for the single crystalline YbTiO₃. The maximal magnetic entropy changes at the second order magnetic phase transition temperature $T_C$ (42 K) are about 2.47 and 5.25 J kg⁻¹ K⁻¹ under 1.5 and 5 T, respectively. The magnetic entropy change is attributed to the sharp magnetization jump, related with anomalies of the lattice parameters just at the Curie temperature. The magnetic entropy change for YbTiO₃ can be well described by a phenomenological universal curve behavior. The field dependence of the magnetic entropy change and the relative cooling power was also studied. From the analysis of the relationship between the local exponent $n$ and the critical exponents, we conclude that the critical behavior of YbTiO₃ belongs to the three-dimensional Heisenberg class, which was also confirmed by the heat capacity measurement.

1. Introduction
Magnetic refrigeration, based on the magnetocaloric effect (MCE), is advantageous being an environment friendly and energy efficient refrigeration mechanism, which is expected to be an important future cooling technology [1, 2]. In recent years, the magnetic materials with large MCEs have been extensively studied experimentally and theoretically, due to their great potential for magnetic refrigeration applications and the further understanding of the fundamental physical properties of the materials [1-8]. The isothermal magnetic entropy change ($\Delta S_M$) and the relative cooling power ($RCP$) are important parameters for evaluating the refrigerant properties [3]. Currently, large MCE has been found in materials with first order magnetic phase transition. However, some of disadvantages such as hysteresis loss should be overcome before using those materials as magnetic refrigerants. Actually, the cooling power of a magnetic refrigerator is a product of the operation frequency and the relative cooling powder of the refrigerant. Therefore, although the materials with
second order phase transition may have a smaller magnetic entropy change, which can be compensated by their faster response, this can facilitate the increase in the operation frequency in refrigerator appliances [4].

Recently, the investigation of the magnetic field \((H)\) dependence of MCE has been renewed in materials with the second order phase transition [5, 6]. Furthermore, the universal curve is fulfilled for \(\Delta S_M\) curves measured at various field changes in amorphous alloys [7]. Later on, the universal behavior may be used as a further criterion to distinguish the order of the phase transition [8]. From a theoretical point of view, the universal curve can be derived from the equation of state and the critical exponents of the system. Scaling laws of the MCE in second order phase transitions have also been proposed, however, the relationship between the critical behavior (i.e. universality class) and the MCE has been studied rarely [9]. In this work, the MCE in YbTiO\(_3\) single crystal was studied. The field dependence of the magnetic entropy change \((\Delta S_M)\) and the relative cooling power \((RCP)\) was also reported. From analyzing the scaling relations, the critical behavior of YbTiO\(_3\) belongs to the three-dimensional Heisenberg universality class.

2. Experimental
Single crystal YbTiO\(_3\) was grown using the floating zone method as described in Ref. [10]. The magnetization measurements were carried out using a commercial Quantum Design Physical Property Measurement System (PPMS-9T). The magnetic entropy change was evaluated from magnetization isotherms for temperature between 10 and 90 K. The heat capacity measurements have also been performed in PPMS with an automated thermal relaxation calorimeter.

3. Results and discussion
The temperature dependence of the magnetization for the YbTiO\(_3\) single crystal was shown in Fig. 1, which was recorded in a magnetic field of 0.01 T upon heating after zero-field cooling (ZFC). YbTiO\(_3\) has a ferrimagnetic ground state below the \(T_C\) for the localized Ti\(^{3+}\) \((S = 1/2)\) spins antiferromagnetically coupled with the Yb\(^{3+}\) moment at low temperature. With decreasing the temperature the decreasing in magnetization at the low temperature region is originated from the anti-parallel alignment of the Yb\(^{3+}\) magnetic moment relative to Ti\(^{3+}\) sublattice. The abrupt drop in magnetization around \(T_C\) corresponding to the magnetic transition from ferrimagnetic to paramagnetic state, leads to a large magnetic entropy change in this compound. In addition, it can be seen that the field cooled cooling (FCC) and field cooled warming (FCW) curves (inset of Fig. 1) all most followed the same path in a large temperature range around the transition temperature, exhibiting no thermal hysteresis loop, indicative of a second order transition.
Isothermal magnetization measurements were performed between 10 and 90 K and a set of isothermal magnetization ($M$) curves for a few selected temperatures in the vicinity of Curie temperature were shown in Fig. 2. The $M$ versus $H$ loops were also measured at different temperatures (inset of Fig. 2). Obviously, there is no magnetic hysteresis in each loop, indicating the perfect reversibility of the magnetic entropy change in YbTiO$_3$ single crystal. To further understand the nature of the magnetic transition in YbTiO$_3$, the Arrott plots $M^2$ versus $H/M$ at some selected temperatures for YbTiO$_3$ are plotted in Fig. 3. Neither the inflection point nor negative slopes are observed, providing the occurrence of a second order magnetic transition for YbTiO$_3$ [11].

![Figure 3. Arrott plots of YbTiO$_3$ from 37 K (top) - 47 K (bottom) with a temperature interval of 0.5 K.](image)

![Figure 4. Magnetic entropy change as a function of temperature under various magnetic field changes. Inset: Master curve behavior for YbTiO$_3$.](image)

Based on the method described by Pecharsky and Gschneider [12], the magnetic entropy change was calculated for YbTiO$_3$ from 10 to 90 K up to 5 T and is shown in Fig. 4. The maximal magnetic entropy changes at the second order magnetic phase transition temperature $T_C$ (42 K) are about 2.47 and 5.25 J kg$^{-1}$ K$^{-1}$ under 1.5 and 5 T, respectively. The magnetic entropy change is attributed to the sharp change of magnetization, related with anomalies of the lattice parameters just at the Curie temperature [13]. A phenomenological universal curve for the field dependence of $\Delta S_M$ has also been constructed in the inset of Fig. 4, which was applied to some magnetic alloys [7, 14]. It is shown that these curves are unique for each universality class [15]. The MCE data of different materials of same universality class should fall onto the same curve irrespective of the applied magnetic field. Because of the intrinsic relation between the MCE and the universality class, one can obtain the critical exponents based on the MCE data, which may be another method to determine the critical behavior of phase transition, i.e. the universality class.

The field dependence of $\Delta S_M^{pk}$ is given by the following equation: $\Delta S_M^{pk} \propto H^n$, where $n = 1 + (\beta - 1) / (\beta + \gamma)$ [15], where $\beta$ and $\gamma$ are the critical exponents. In order to calculate the value of $n$, we first obtain the relation of $\Delta S_M^{pk}$ versus $H$ from Fig. 4, as shown by black squares in Fig. 5. Then, using the above function of $\Delta S_M^{pk} \propto H^n$, the value of $n$ was determined to be $n = 0.633$. Notably, we need to establish another equation to solve $\beta$ and $\gamma$. As we known, the critical exponents of $\beta, \gamma, \text{ and } \delta$ satisfy the Widom scaling relation: $\delta = 1 + \gamma / \beta$. Coincidently, the critical exponent of $\delta$ is associated with the relative cooling power ($RCP$) and can be obtained from the following equation: $RCP \propto H^{1+\delta} [6]$. As shown in Fig. 5, the calculated value of $\delta$ is 4.95. Using the obtained values of $n$ and $\delta$, the values of $\beta$ and $\gamma$ were calculated to be 0.355 and 1.402, respectively. From the values of $\beta, \gamma, \text{ and } \delta$, the critical behavior of YbTiO$_3$ belongs to the three-dimensional Heisenberg universality class. The heat capacity of YbTiO$_3$ is shown in Fig. 6, one can obtain the critical exponent

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of $\alpha$, using the function: $C_p = B + C t + A^2 \left[ t^\alpha \left(1 + E^\alpha \right) \right]^{0.5}$, where $t = (T - T_C)/T_C$; A, B, C and E are the adjustable parameters; superscripts + and – stand for $T > T_C$ and $T < T_C$, respectively. The value of $\alpha$ was determined to be -0.11, which is further confirmed the result of the critical behavior of YbTiO$_3$ belongs to the Heisenberg model. The relationship between the critical behavior (i.e. universality class) and the MCE should be further studied in other compounds.

![Figure 5. The maximal magnetic entropy change and the relative cooling power versus $H$ and the solid lines are the fitting curves.](image)

![Figure 6. The heat capacity versus temperature and the solid line is the fitting curve.](image)

4. Conclusions

In summary, the magnetic entropy change ($\Delta S_M$) and the relative cooling power (RCP) were studied for YbTiO$_3$ single crystal. By using the field dependence of $\Delta S_M$ and RCP, we have investigated the critical behavior of YbTiO$_3$. From the calculated critical exponents, the YbTiO$_3$ belongs to the three-dimensional Heisenberg universality class. This method can be extensively applied to study the critical behavior.

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