Magnetic properties and magnetocaloric effects in antiferromagnetic ErTiSi

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Magnetic properties and magnetocaloric effects (MCEs) of the antiferromagnetic (AFM) ErTiSi compound with a Néel temperature T_N=46 K are studied by magnetization measurements. Two successive magnetic transitions in the thermomagnetic *M-T* curves, an AFM-AFM transition followed by an AFM-paramagnetic transition with increasing temperature, are observed. ErTiSi undergoes a field-induced metamagnetic transition from AFM to FM state below T_N. A sign change in MCE with increasing temperature or magnetic field in ErTiSi is observed near the critical field. The maximal value of magnetic entropy change ΔS_m is −8.9 J/kg K around T_N for a field change of 0–5 T. The modest ΔS_m as well as no hysteresis loss around T_N in ErTiSi may be useful for its application in magnetic refrigeration. © *2010 American Institute of Physics*.
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I. INTRODUCTION

Magnetic refrigeration based on the magnetocaloric effect (MCE) of materials is a potential technique that has prominent advantages over the currently used gas compression-expansion technique in the sense of its high efficiency and environment friendship.[1–3] However, the development of magnetic refrigeration technology depends on the discovery and the synthesis of novel magnetic materials that possess large MCEs. In order to obtain a large MCE, the magnetic materials are usually required to possess large enough spontaneous magnetization and strong temperature dependence of magnetization around their phase transition temperatures. Therefore, many investigations on magnetic refrigeration have concentrated on rare earth (*R*) intermetallic compounds and crystalline materials with a first-order phase transition. The giant MCEs have been observed in many materials that experience a first-order magnetic or structural phase transition, such as $Gd_5Si_2Ge_2$,[4] $ErCo_2$,[5] $LaFe_{13-x}Si_x$,[6] $MnFeP_{1-x}As_x$,[7] $Ni_{0.5}Mn_{0.5-x}Sn_x$,[8] etc. Recently, much attention has been also paid to the *R*-based intermetallic compounds with a low-temperature phase transition for the purpose of magnetic refrigerant application. In fact, magnetic materials exhibiting a large MCE at temperatures below 70 K are potential magnetic refrigerants for the gas liquefiers.[2,3] Some *R*-based compounds with a ferromagnetic (FM) or antiferromagnetic (AFM) phase transitions, such as ErNiAl,[9] RCoAl,[10] Gd_3T (*T*=Co and Ni),[11] $Pr_6Co_{1.67}Si_3$,[12] and DySb,[13] have been found to possess not only large magnitude of magnetic entropy change and/or adiabatic temperature change but also quite a small hysteresis loss, which are just required by magnetic refrigerant materials. In the previous studies, a family of ternary *R*TiSi (Y and Gd–Er) compounds was discovered by Morozkin,[14] and these compounds crystallize in the tetragonal CeFeSi-type structure (space group P4/nmm). The crystal structure, phase transition, and magnetic properties of *R*TiSi have been studied in detail by using neutron diffraction and magnetic measurements.[14–17] It was found that the GdTiSi undergoes a FM ordering below the Curie temperature T_C=294 K,[15] whereas the *R*TiSi (Tb–Tm) compounds behave antiferromagnetically and exhibit different AFM structures below the Néel temperature T_N.[17] The magnetic structure of the *R*TiSi (Tb, Dy, Ho, and Er) compounds consists of FM (0 0 1) *R* layers antiferromagnetically coupled along the c-axis with the (++−−) coupling sequence.[17] The interesting magnetic structure and large *R* magnetic moment in *R*TiSi compounds makes them good candidates for the study of MCE. In the present paper, we report the results of MCE study of ErTiSi compound.

II. EXPERIMENTAL DETAILS

Polycrystalline ErTiSi sample was prepared by arc melting appropriate proportions of raw materials of Er and Ti (99.9% in purity) and Si (99.99%) in an atmosphere of high-purity argon. The ingot was turned over and remelted several times to ensure its homogeneity. Ingots obtained by arc melting were wrapped by molybdenum foil, sealed in a quartz tube of high vacuum, annealed at 1273 K for 16 days and then quenched to room temperature. Powder x-ray diffraction (XRD) measurements were performed using Cu Kα radiation to identify the phase structure and the crystal lattice parameters. Magnetizations were measured as functions of temperature and magnetic field by using a superconducting quantum interference device magnetometer. The sweep rate of the field was quite slow to ensure that the *M-H* curves could be recorded in an isothermal process.

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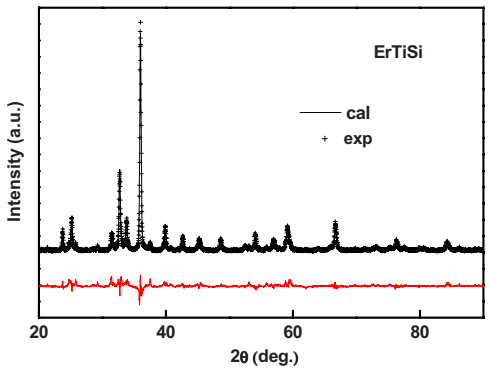

FIG. 1. (Color online) Rietveld refined powder XRD pattern of ErTiSi at room temperature. The observed data are indicated by crosses and the calculated profile is the continuous line overlying them. The lower curve is the difference between the observed and calculated intensities.

III. RESULTS AND DISCUSSION

Figure 1 shows the Rietveld refined powder XRD patterns of ErTiSi at room temperature. All the diffraction peaks can be indexed to a tetragonal CeFeSi-type structure (space group P4/nmm). However, small amounts of a second phase, up to ~5 vol % could be present. The lattice parameters a and c were determined to be 0.4004(9) and 0.7480(8) nm, respectively, by using the Rietveld refinement method, which is in good agreement with the value reported in Ref. 17.

Figure 2 shows the magnetization (M) and the reciprocal magnetic susceptibility χ_m^{-1} versus temperature for ErTiSi in a field of 1 T. It is found that there are two successive magnetic transitions in the M-T curves. A similar result was also observed in ErTiGe compound.[18,19] The anomaly at low temperature (T_{AF}=~9 K) may be associated with a possible change from collinear to noncollinear AFM structure.[19] The transition at a higher temperature corresponds to a change from AFM to paramagnetic (PM) state with increasing temperature, and its Néel temperature T_N is determined to be 46 K. It is also found from Fig. 2 that the magnetic susceptibility of the ErTiSi compound at temperatures above ~65 K perfectly follows the Curie–Weiss law $\chi_m^{-1}=(T-\theta_p)/C_m$, where θ_p is the PM Curie temperature and C_m is the Curie–Weiss constant. The value of θ_p for ErTiSi is positive and equals 29.1 K. From the value of C_m, the effective magnetic moment μ_{eff} per Er atom is obtained and its value is 9.79 μ_B, which is close to the value expected for a free Er^{3+} ion (μ_{eff}=9.59 μ_B).

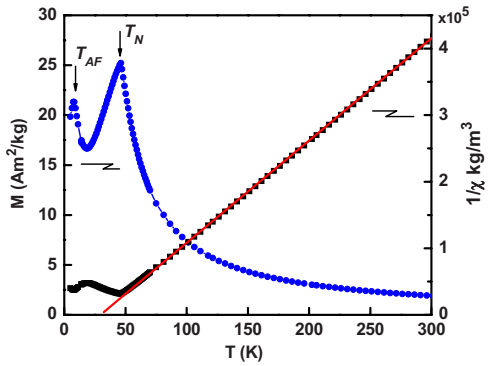

FIG. 2. (Color online) Magnetization and the reciprocal magnetic susceptibility vs temperature for ErTiSi under a magnetic field of 1 T.

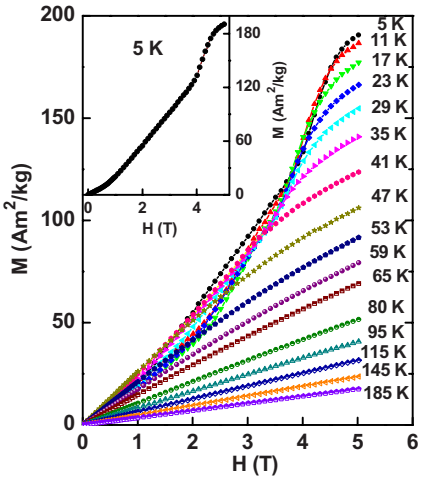

FIG. 3. (Color online) Isothermal magnetization curves for ErTiSi in a temperature range of 5–185 K under the magnetic fields up to 5 T. The inset shows the magnetization isotherms of ErTiSi at 5 K.

Figure 3 shows the isothermal magnetization curves for ErTiSi in the temperature range of 5–185 K under the magnetic fields up to 5 T. It can be seen from Fig. 3 that there is considerable difference in the M-H characteristics for ErTiSi in different temperature ranges. In the ~65–185 K temperature ranges, the field dependence of the magnetization shows a linear relation, whereas the isothermal curves for $T_N<T<$~65 K show an appreciable nonlinearity. The curvatures in the M-H curves above T_N probably indicate the existence of short-range FM correlations in the PM state, which is in agreement with the result of positive θ_p for ErTiSi (see Fig. 2). The positive value of θ_p implies the presence of FM interactions in ErTiSi compound because θ_p reflects the collective exchange interactions in the compound. It can also be seen from Fig. 3 that the isothermal magnetization curves of ErTiSi do not really saturate even under magnetic field of 5 T and exhibit a nonlinearly positive field gradient below T_N. The successive field-induced transitions in ErTiSi in the temperature range of 5–43 K are observed as expected for an antiferromagnet with a possible metamagnetic transition at higher fields. This result resembles the previous reports on $DyCu_2$ single crystals,[20,21] in which the successive field-induced transitions from an AFM phase to another AFM phase, and then to a FM phase was observed at low temperatures. From the M-H data for ErTiSi at 5 K (see the inset in Fig. 3), it is found that this compound undergoes a possible field-induced AFM-AFM phase transition at about 0.8 T, and then to an AFM-FM metamagnetic transition at a critical field of ~4 T, giving rise to a field-induced FM state. The value of Er magnetic moment at 5 K for a magnetic field of 5 T is found to be 8.3 μ_B, which is slightly lower than the free-ion value for Er^{3+} (9.0 μ_B). To investigate the reversibility of the magnetic transitions in ErTiSi, the M-H curves below T_N in field increasing and decreasing modes were also measured. Almost no magnetic hysteresis in each curve is observed, indicating that the magnetization of ErTiSi around T_N is perfectly reversible.

In an isothermal process of magnetization, the magnetic entropy change ΔS_m in the materials can be derived from the Maxwell relation $\Delta S_m=\int_0^H(\partial M/\partial T)_H dH$. To derive the temperature dependence of magnetic entropy change, the follow-

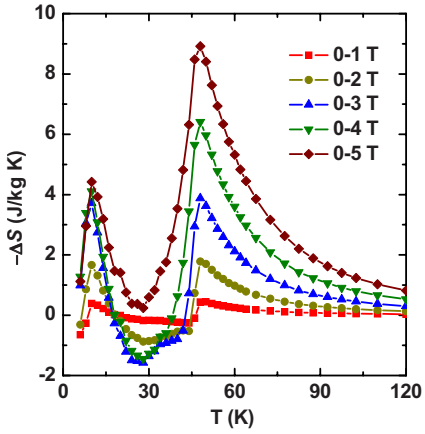

FIG. 4. (Color online) Magnetic entropy change as a function of temperature of ErTiSi for different magnetic field changes up to $H=5$ T.

ing numerical approximation of the integral is usually adopted under increasing and decreasing fields,

$$|\Delta S_m| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H_i, \quad (1)$$

where M_i and M_{i+1} are the experimental values of the magnetization measured at T_i and T_{i+1} in an applied magnetic field H_i, respectively. We calculate ΔS_m associated with the H variation for ErTiSi according to expression (1). Figure 4 shows ΔS_m as a function of temperature for different magnetic field changes up to $H=5$ T. It is observed that the values of $-\Delta S_m$ for ErTiSi are negative (inverse MCE) at low temperatures, but they change to positive value with the increase in temperature or magnetic field. A sign change in MCE in ErTiSi is associated with the field-induced metamagnetic transition from AFM to FM state below T_N. Moreover, the ΔS_m peak around T_N broadens asymmetrically toward higher temperatures with increasing magnetic field, which also indicates a result of the field-induced IEM transition.[22] It also can be observed in Fig. 4 that two peaks in the $\Delta S_m - T$ curves are centered at 10 and 48 K, respectively, corresponding to the two transitions at T_{AF} and T_N in the M-T curves. It is found that ΔS_m of ErTiSi depends on the applied magnetic field and increases obviously with increasing field. For a field change of 0–5 T, $-\Delta S_m$ reaches a maximal value of 8.9 J/kg K at 48 K, which is much less than those of some potential magnetic refrigerant materials in similar magnetic transition temperatures, such as $(Dy_{0.7}Er_{0.3})Al_2$ (19 J/kg K at 47.5 K),[3] $ErCo_2$ (~32 J/kg K at 37 K),[3] $Ho(Co_{0.9}Ni_{0.1})_2$ (22 J/kg K at 40 K),[23] and TbNiAl (13.8 J/kg K at 47 K).[24] However, this value is comparable to those of $Pr_6Co_{1.67}Si_3$ (6.9 J/kg K at 48 K),[12] $DyAl_2$ nanoparticles (8.45 at ~40 K),[25] and Gd_2Al (7.2 J/kg K at ~50 K).[26] The maximal value of ΔS_m for ErTiSi is also much larger than that for AFM ErTiGe compound,[19] which has a ΔS_m of −0.75 J/kg K at 39 K for a field change of 0–5 T. The ErTiSi compound exhibits a better MCE than the ErTiGe compound, which may be due to a stronger field-induced AFM to FM transition in ErTiSi below T_N.

IV. CONCLUSIONS

In summary, we have studied the magnetic and magnetocaloric properties of ErTiSi compound, which shows a Néel temperature $T_N=46$ K. It is observed that the magnetization of ErTiSi is strongly affected by temperature and magnetic field below T_N. ErTiSi exhibits a modest $-\Delta S_M$ of 8.9 J/kg K around T_N for a field change of 0–5 T, which results from the field-induced metamagnetic transition from AFM-to-FM state. The maximal value of ΔS_m for ErTiSi is over an order of magnitude larger than that of ErTiGe compound due to stronger FM interactions caused by the field-induced metamagnetic transition in ErTiSi.

ACKNOWLEDGMENTS

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