Magnetocaloric Effect in ErSi Compound

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The magnetic properties and magnetocaloric effects (MCEs) have been investigated in ErSi compound, which crystallizes in the orthorhombic CrB-type structure. This compound is antiferromagnetic (AFM) with a Néel temperature T_N of 12.5 K. The measurements of the temperature and field dependences of the magnetization clearly show that the ErSi compound undergoes a field-induced metamagnetic transition from AFM to ferromagnetic (FM) state below T_N. The isothermal magnetic entropy change (ΔS_M) and refrigerant capacity (RC) of ErSi have been measured for various applied magnetic fields and their values are found to be $-14.8 \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$ and $210 \mathrm{J \cdot kg^{-1}}$ for a field change of 0–5 T, respectively. The large MCE is attributed to the field-induced AFM to FM metamagnetism occurring in this compound.

Index Terms—Antiferromagnetic (AFM) materials, magnetocaloric effect (MCE), magnetic refrigeration.

I. INTRODUCTION

MAGNETIC refrigeration based on magnetocaloric effect (MCE) is a promising cooling strategy due to its higher energy efficiency and environment friendly compared to the conventional gas compression-expansion technology [1]–[4]. The search for working substances in the temperature range of interest is a significant aspect of magnetic refrigeration investigation. Giant magnetocaloric performances around the transition temperatures have been found in many materials with a first-order phase transition, such as $Gd_5(Si,Ge)_4$ [5], $La(Fe,Si)_{13}$ [6], [7], $MnFeP_{0.45}As_{0.55}$ [8], $Ni_{51.5}Mn_{22.7}Ga_{25.8}$ [9], etc. The MCE has been used for years to obtain ultralow temperatures through demagnetization of paramagnetic (PM) salts [10]. Liquefaction of hydrogen or helium is fundamental for many industrial and science applications. Recently, much attention has also been paid to the rare-earth (R) based intermetallic compounds with low-temperature phase transitions for the purpose of magnetic refrigerant application.

It has been reported that the ferrimagnet $ErCo_2$, which shows a first-order magnetic transition between ferrimagnetic and PM state at 32 K, exhibits a giant MCE [11]. Recently, the antiferromagnetic (AFM) Ni_2 In-type HoCuSi compound is found to have a giant reversible MCE, which results from the field-induced AFM to ferromagnetic (FM) transition below Néel temperature (T_N) and the increase in magnetization change caused by the change in lattice volume at T_N [12]. The research of these materials not only extend the variety of magnetocaloric materials but also stimulate our research on the MCE of R-based compounds for potential magnetic refrigerant.

The structure and magnetic properties of various rare-earth silicon intermetallic compounds have been studied. The RSi compounds are found to have an orthorhombic FeB-type or CrB-type crystal structure, and are known to be AFM at low temperatures [13], [14]. Reference [15] has presented the
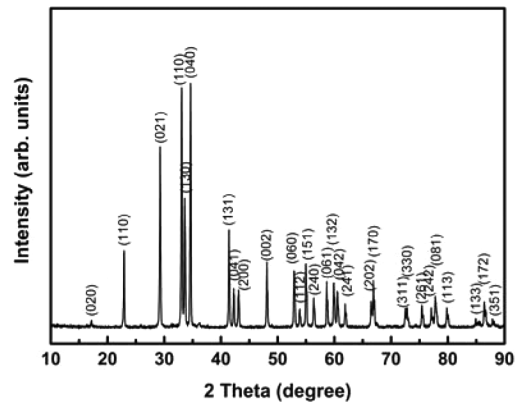
Fig. 1. XRD pattern of ErSi at room temperature.

MCE of the AFM DySi. In the present work, we show that the field-induced metamagnetic transition from AFM to FM state below T_N observed in ErSi lead to a large MCE around the T_N and an interesting change from negative to positive MCE caused by the strong temperature and field dependence of magnetization.

II. EXPERIMENTS

Polycrystalline ErSi was prepared by arc melting constituent elements in a high-purity argon atmosphere. The purities of starting materials were better than 99.9%. The ingot was turned over and remelted four times to ensure its homogeneity. The sample was wrapped in a molybdenum foil, annealed at 1223 K for one week in an evacuated quartz tube, and then quenched into liquid nitrogen. X-ray diffraction (XRD) measurements on powder samples were performed by using Cu Kα radiation to identify the crystal structure and the phase purity. The magnetization was measured as functions of temperature and magnetic field by using a MPMS-XL 7 T from Quantum Design.

III. RESULTS AND DISCUSSION

In Fig. 1, the variation of diffraction intensity with diffractive angle (XRD pattern) measured at ambient temperature is
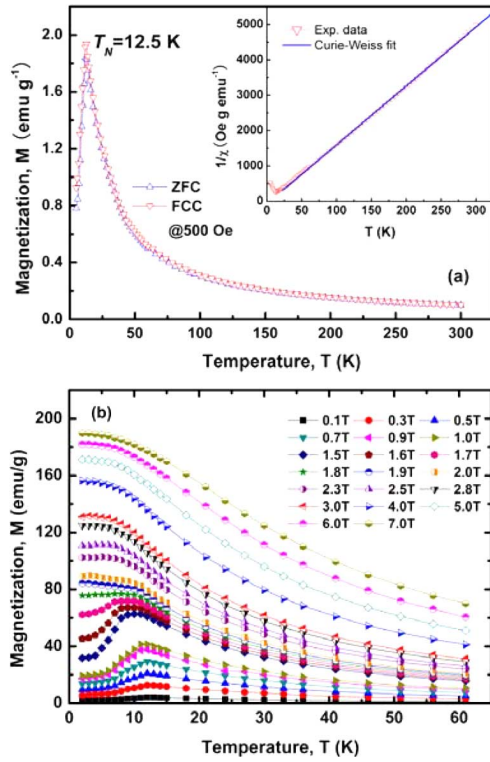
Fig. 2. (a) Temperature dependences of the zero field cooling (ZFC) and field cooled cooling (FCC) magnetization of ErSi under a magnetic field of 500 Oe. The inset shows the inverse of the FCC susceptibility $(1/\chi)$ as a function of temperature. (b) Temperature dependences of the magnetization under selected magnetic fields at low temperature.

shown. The further Rietveld refinement confirms that the prepared sample is of single phase with a CrB-type structure belonging to space group *Cmcm*.

Fig. 2(a) shows the temperature (T) dependence of the magnetization (M) of ErSi, measured in both zero field cooling (ZFC) and field cooled cooling (FCC) mode under a field of 500 Oe. Clearly, the ErSi compound experiences a magnetic transition from AFM to PM state as temperature increases and its Néel temperature T_N is about 12.5 K, determined by the position of the peak in the M versus T curves. Earlier susceptibility measurement and neutron diffraction studies have reported a T_N of ~10 K and ~11.5 K, respectively [16], [17]. One can see that there is superposition between ZFC and FCC $M - T$ curves above T_N, indicating the occurrence of a reversible thermomagneitc process occurs. The inverse FCC susceptibility $(1/\chi)$ as a function of temperature at 500 Oe magnetic field derived from the magnetization data is presented in the inset of Fig. 2(a). It is found that the inverse susceptibility of ErSi at temperatures above ~65 K perfectly obeys the Curie–Weiss law. The gradient of this curve, obtained by fitting a straight line, gives the Curie–Weiss constant (C) for ErSi. This constant C is related to the effective magnetic moment (μ_{eff}) of the material in the PM state. The value of the effective magnetic moment per Er ion for ErSi is 9.6 μ_B, which is very close to $\mu_{\text{eff}} = 9.59\,\mu_B$ for the free Er^{3+} ion. The PM Curie temperature (θ_p) is estimated to be about 6.5 K. The positive θ_p value actually indicates ferromagnetic coupling prevailing for the magnetic moments localized on Er ions. Fig. 2(b) shows the temperature dependence
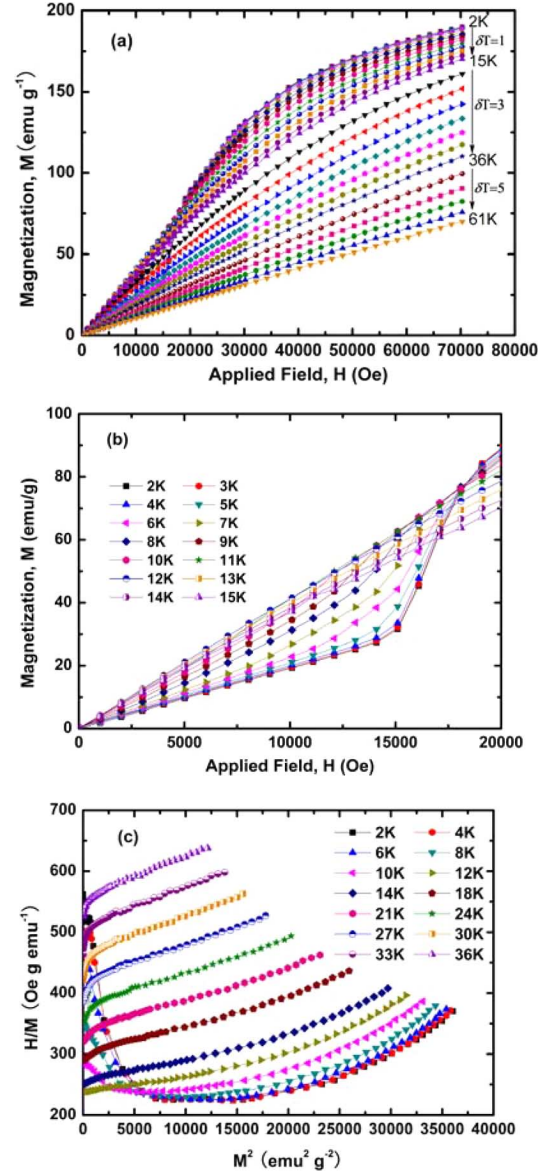

Fig. 3. (a) Isothermal magnetization as a function of applied magnetic field up to 7 T in a range of 2–61 K in different temperature steps. (b) The variation of the magnetization with temperature in low temperature range. (c) Arrott plots of ErSi in selected temperature.

of the magnetization at different magnetic fields. It is apparently seen that the magnetization at low temperatures increases greatly with increasing field, indicating a field-induced metamagnetic transition from AFM to FM state below T_N. When the applied magnetic field is higher than about 1.8 T, the magnetization as a function of temperature for ErSi exhibits steplike behavior above T_N, which corresponds to the FM to PM transition. Similar results have also been observed in DySb [18], $DyCu_2$ [19] and DyCuSi [20].

Fig. 3(a) shows isothermal magnetization (M) versus applied field (H) curves measured around T_N in a temperature range of 2–61 K with different temperature steps and a maximum applied field of 7 T. It is observed that there is a considerable difference in the M versus H of ErSi in different temperature regimes. The magnetization below T_N is found to increase linearly with increasing magnetic field in low field ranges, as shown in Fig. 3(b),

revealing the AFM ground state of the compound. However, it is found that the magnetization exhibits a sharp increase when the applied field exceeds a certain value, indicating that the field-induced matamagnetic transition from AFM to FM state occurs. However, one can find that even at 2 K, the curve does not really saturate in 7 T magnetic field and exhibits a strong positive field gradient. The critical field required for metamagnetism for ErSi is observed to be about 1.62 T at 2 K, showing that the compound is a strong antiferromagnet. On the other hand, the field dependence of the magnetization for temperatures much higher than T_N shows a linear relation. However, the isothermal magnetization curves obtained well above T_N show an appreciable nonlinearity. The curvature in the M versus H curves indicates the existence of short-range ferromagnetic correlations in the PM state. Similar results have been observed in many other compounds [21], [22].

The H/M versus M^2 curves, i.e., Arrott plots of the ErSi compound at selected temperatures are shown in Fig. 3(c). According to the Banerjee criterion [23], a magnetic transition is expected to be of the first order when the slope of the Arrott plot is negative, whereas it will be of the second order when the slope is positive. It can be obviously seen from Fig. 3(c) that the negative slope of the Arrott plot for ErSi below T_N confirms the first-order AFM to FM transition. However, the positive slope above T_N indicates the characteristic of a field-induced second-order PM to FM transition.

One of the most important parameters for evaluating the potentiality of a magnetic refrigeration material is the isothermal magnetic entropy change (ΔS_M), which is expected to achieve its maximum at the transition point. In an isothermal process of magnetization, the ΔS_M can be derived from the Maxwell relation by integrating the magnetization over the applied magnetic field, i.e.,

$$\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH. \tag{1}$$

To derive the temperature dependence of magnetic entropy change, the following numerical approximation of the integral is practically adopted under variational fields:

$$\Delta S_M = \sum_i \frac{M_{i+1} - M_i}{T_{i+1} - T_i} \Delta H_i \tag{2}$$

where M_i and M_{i+1} are the experimental magnetization measured at the temperature T_i and T_{i+1} in an applied magnetic field H_i, respectively. For ErSi, we calculate the ΔS_M associated with the field variation according to expression (2). Fig. 4 shows the temperature dependence of ΔS_M at different magnetic field changes. It is observed that both the ΔS_M peaks and the width of ΔS_M peaks depend on the applied magnetic field, and increase obviously with filed increasing. The ΔS_M peak in ErSi is found to broaden asymmetrically toward high temperatures with the increase of magnetic field, resulting in a large MCE in the temperature above T_N. It is found that the values of $-\Delta S_M$ for ErSi are negative at temperatures below T_N and at lower magnetic field, but they change to a positive value with the increase of applied field due to the field-induced magnetic transition from
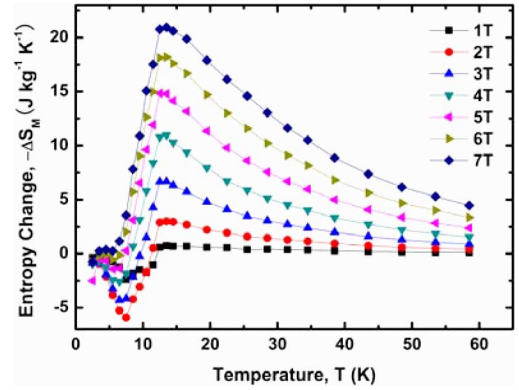

Fig. 4. Temperature dependences of isothermal magnetic entropy change in ErSi for different applied magnetic field changes.

AFM to FM state. The positive ΔS_M (negative MCE) is often observed in magnetocaloric materials with the first-order magnetic transitions, which results from the mixed exchange interaction, and the applied magnetic field leads to a further spin-disordered state near the transition temperature, thereby increasing the configurational entropy [24]. A large ΔS_M, which results from the field-induced AFM-FM metamagnetic transition, is observed in ErSi around T_N. The maximal ΔS_M values in ErSi are achieved to be -14.8 and -21 J·kg^{-1}·K^{-1} for field changes of 0–5 and 0–7 T, respectively, which is comparable to those of some magnetic refrigeration materials in a similar transition temperature under the same field change, such as ErNi$_5$ (15 J·kg^{-1}·K^{-1}) [25], DySb (15.8 J·kg^{-1}·K^{-1}) [18]. The large ΔS_M results from the high saturation magnetization caused by the field-induced AFM to FM metamagnetic transition. As is known, it is not sufficient to identify the potentiality of a magnetic material solely by the ΔS_M. Another important parameter is refrigerant capacity (RC), a measure of how much heat can be exchanged between the cold and hot parts in a thermodynamic cycle. The RC of ErSi has been estimated by using the approach suggested by Gschneidner *et al.* [26]. The RC is defined as

$$RC = \int_{T_1}^{T_2} |\Delta S_M| dT \tag{3}$$

where T_1 and T_2 are the temperatures corresponding to both sides of the half-maximum value of ΔS_M peak, respectively. The value of RC for ErSi calculated by numerically integrating the area under the $\Delta S_M - T$ curve is 210 J·kg^{-1} for a field change of 0–5 T. It is evident that the large RC is due to the high ΔS_M value and the relatively wide ΔS_M peak.

IV. CONCLUSION

In summary, the ErSi compound with orthorhombic CrB-type structure undergoes an AFM transition at ∼12.5 K and a field-induced first-order metamagnetic transition from AFM to FM state below T_N. The maximal values of ΔS_M are achieved to be -14.8 and -21 J·kg^{-1}·K^{-1} for field changes of 0–5 and 0–7 T, respectively. The estimated RC value is 210 J·kg^{-1} for a field change of 0–5 T.

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