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Giant magnetic entropy change in antiferromagnetic DyCuSi compound

J. Chen, B.G. Shen[*], Q.Y. Dong, J.R. Sun

State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing, 100190, People's Republic of China

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ABSTRACT

Magnetic properties and magnetocaloric effects (MCE) of intermetallic DyCuSi compound have been investigated by means of magnetization measurements. It is found that DyCuSi is an antiferromagnet with a Néel temperature $T_N = 10$ K and undergoes a field-induced metamagnetic transition from antiferromagnetic to ferromagnetic states below T_N. The MCE around T_N has been studied by using the field-dependent magnetization data. The maximal magnetic entropy change ($-\Delta S_M$) and refrigerant capacity (RC) are 24.0 J/kg K and 381 J/kg, respectively, for the field change of 0–5 T. The giant ΔS_M without hysteresis loss around T_N is found to result from the field-induced metamagnetic transition.

1. Introduction

The temperature increase (decrease) of material in response to applying (removing) an external magnetic field adiabatically is called the magnetocaloric effect (MCE). Magnetic refrigeration based on the MCE is expected to be a promising alternative technology to the conventional gas compression refrigeration due to its higher energy efficiency and friendly environment [1–4]. To improve the application of this cooling technology, many efforts have been made to explore advanced magnetic refrigerant materials with large MCE, i.e. large magnetic entropy change (ΔS_M) and high adiabatic temperature (ΔT_{ad}). Numerous ferromagnetic materials have been found to exhibit giant ΔS_M around their transition temperatures due to the sharp change in magnetization in a narrow temperature interval, which is usually associated with the first-order magnetic or structural phase transition [5–12]. However, the majority of them are less efficient in the fast-cycling refrigerator because the considerable thermal and magnetic hysteresis and the slow kinetic inherence in first-order magnetic transition can greatly reduce the actual refrigerant capacity (RC) of the materials. Therefore, it is necessary to acquire efficient magnetic materials with a large reversible MCE. Recently, some antiferromagnetic materials, such as $ErRu_2Si_2$ [13], DySb [14], and $GdCo_2B_2$ [15], have been found to possess not only giant MCEs but also quite a small hysteresis loss, which are just required by magnetic refrigerant materials. In the present paper, we report a large reversible MCE in antiferromagnetic DyCuSi compound. The maximal values of $-\Delta S_M$ for DyCuSi are 10.5 and 24.0 J/kg K for the magnetic field changes of 0–2 T and 0–5 T, respectively. The excellent magnetocaloric properties in DyCuSi is believed to be associated with the field-induced metamagnetic transition from antiferromagnetic (AFM) to ferromagnetic (FM) state below T_N.

2. Experiments

Polycrystalline DyCuSi was prepared by arc melting the constituent elements of purity better than 99.9% in a high-purity argon atmosphere. The sample was turned and remelted four times to ensure homogeneity. The obtained ingots each was wrapped by a molybdenum foil, sealed in a high-vacuum quartz tube, annealed at 850 °C for 1 week and then quenched into liquid nitrogen. X-ray diffraction (XRD) measurements on powder samples were performed by using Cu Kα radiation to identify the phase structure and the crystal lattice parameters. The Rietveld refined XRD pattern of DyCuSi is shown in Fig. 1. It shows that the sample is a clean single phase with a hexagonal Ni_2In-type structure (space group $P6_3/mmc$). The lattice parameters are $a = 4.136(5)$ and $c = 7.395(3)$ Å. The magnetization was measured as a function of temperature and magnetic field by using a physical property measurement system (PPMS) from Quantum Design.

3. Results and discussion

The temperature dependences of zero-field-cooling (ZFC) and field-cooling (FC) magnetization (M) in the magnetic field of 0.01 T are shown in Fig. 2(a). According to neutron diffraction measurement performed by Oleś et al. [16], DyCuSi is an anti ferromagnet

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[*] Corresponding author. Tel.: +86 10 82648082; fax: +86 10 82649485.
E-mail address: shenbg@g203.iphy.ac.cn (B.G. Shen).

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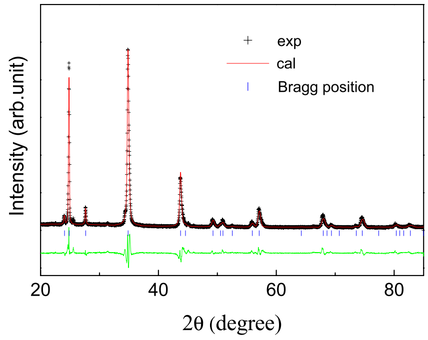

Fig. 1. (Colour on-line) Rietveld refined powder XRD pattern of DyCuSi at room temperature. The observed data are indicated by crosses, and the calculated profile is the continuous line overlying them. The short vertical lines indicate the angular positions of the Bragg peaks of DyCuSi. The lower curve shows the difference between the observed and calculated intensity.

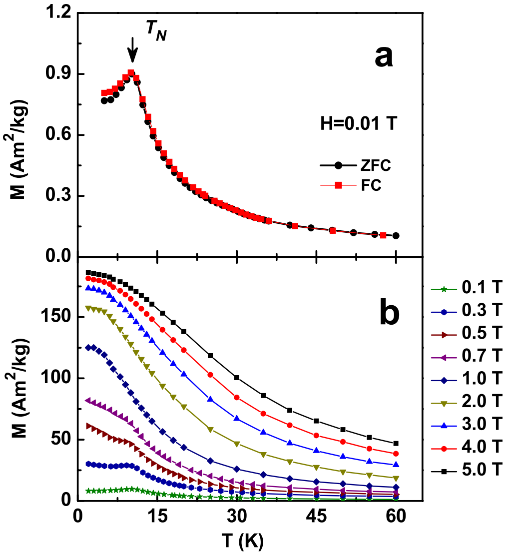

Fig. 2. (Colour on-line) (a) Temperature dependences of the ZFC and FC magnetization of DyCuSi under the magnetic field of 0.01 T. (b) Temperature dependences of the magnetization under different magnetic fields.

with a sine wave modulated structure described by two component propagation vectors. As displayed in Fig. 2(a), the M–T curve for DyCuSi show an AFM-to-PM transition at $T_N = 10$ K. The value of the Néel temperature T_N is close to that reported in Ref. [16]. In addition, it can be seen from Fig. 2(a) that there is almost no hysteresis in ZFC and FC curves above 10 K. Below 10 K, the small difference between the ZFC and FC curves may be related to the domain-wall pinning effect. Fig. 2(b) show the temperature dependences of the magnetization for DyCuSi in different magnetic fields. A field-induced metamagnetic transition from AFM to FM states is clearly observed below T_N and the field-induced modification toward the FM state occurs in a relatively low field range.

Fig. 3(a) displays the isothermal magnetization curves for DyCuSi in a temperature range of 2–45 K under the magnetic fields up to 5 T. It is found that the magnetization of DyCuSi below T_N increases linearly with the increase of the magnetic field in low field ranges and the magnetization is smoothly saturated in high field ranges. For temperatures much higher than the T_N, the field dependence of the magnetization shows a linear relation. Further analysis on magnetization data find that the temperature dependence of $\mathrm{d}M/\mathrm{d}H$ below T_N exhibits clearly a maximum value as shown in Fig. 3(b), revealing also the field-induced metamagnetic transition from AFM to FM states. The critical magnetic field, which is determined from the maximum of the $\mathrm{d}M/\mathrm{d}H$ curve, is found to increase monotonically with the decrease of temperature and reaches a value of 0.45 T at 2 K (see the inset of Fig. 3(b)). The negative slope of the Arrott plots below T_N, which is shown in Fig. 3(c) and the inset, further confirms the occurrence of the AFM-to-FM metamagnetic transition [17].

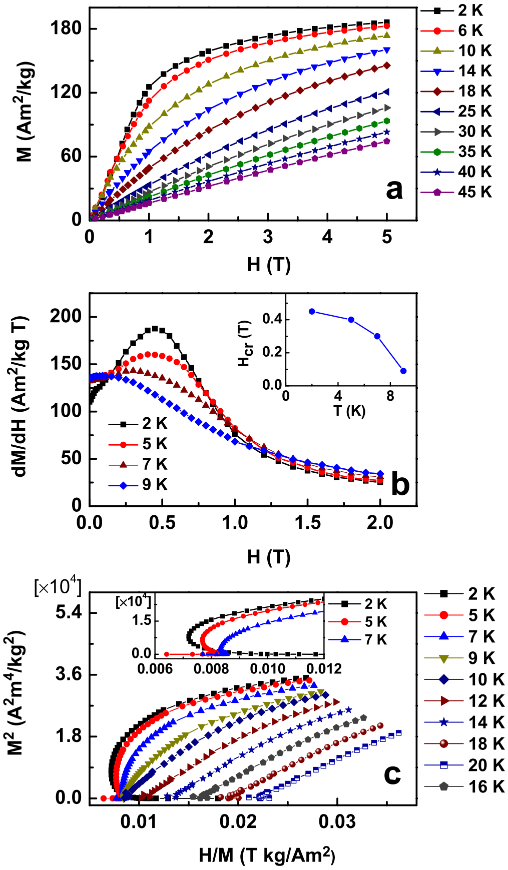

Fig. 3. (Colour on-line) (a) Magnetic isotherms of DyCuSi in a temperature range of 2–45 K in different temperature steps. (b) Magnetic field derivatives of magnetization data ($\mathrm{d}M/\mathrm{d}H$) as a function of the magnetic field at different constant temperatures. Inset: the temperature dependence of the critical magnetic field. (c) Arrott plots of DyCuSi at temperatures near T_N. Inset: the Arrott plots at temperatures of 2, 5, and 7 K, respectively.

The magnetic hysteresis loop for DyCuSi measured at 5 K is shown in Fig. 4. Almost no magnetic hysteresis is observed (see the inset of Fig. 4), indicating the perfect magnetic reversibility of DyCuSi compound. As is known, a completely reversible MCE requires no hysteresis in magnetization as a function of both temperature and magnetic field. For the present sample, such a case is advantageous to practical applications of the materials.

The magnetic entropy change of DyCuSi was calculated from magnetization isotherms shown in Fig. 3(a) by using the Maxwell relation $\Delta S_M = \int_0^H (\partial M/\partial T)_H \mathrm{d}H$ [18]. Fig. 5 shows the temperature dependences of $-\Delta S_M$ for different magnetic field changes. It is seen clearly that the $-\Delta S_M$ of DyCuSi has a small negative value at a lower temperature, but it changes to a positive value with the increase of the magnetic field, corresponding to the magnetic transition from AFM to FM states. A giant magnetic entropy change results from the field-induced metamagnetic transition in DyCuSi around T_N. The maximal value of $-\Delta S_M$ is found to be 24.0 J/kg K at T_N for a magnetic field change from 0 to 5 T, which is comparable with or larger than those of some potential magnetic refrigerant materials with reversible magnetic transitions in a similar temperature range, for example antiferromagnetic $ErRu_2Si_2$ (17.6 J/kg K) [13], DySb (15.8 J/kg K) [14], ErNiAl (21.7 J/kg K) [19], $GdPd_2Si$ (15.1 J/kg K) [20], and ferromagnetic $DyNi_2$ (21.4 J/kg K) [21]. Particularly, a large $-\Delta S_M$ value of 10.5 J/kg K is achieved for a low

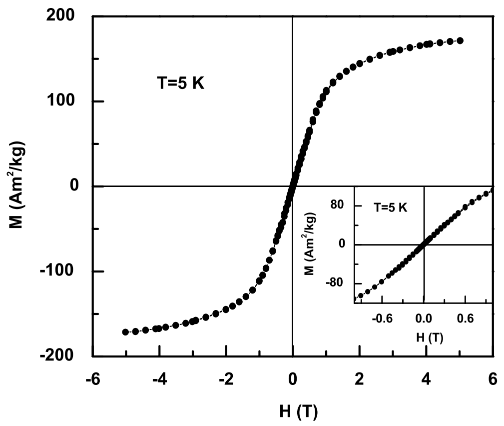

Fig. 4. Magnetic hysteresis loop of DyCuSi at 5 K. Inset: the magnetic hysteresis loop at 5 K in the lower magnetic field region.

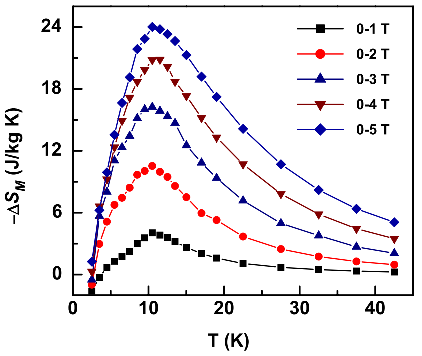

Fig. 5. (Colour on-line) Temperature dependences of magnetic entropy change of DyCuSi for different magnetic field changes.

field change of 2 T that can be realized by permanent magnet, which is advantageous to applications.

It is insufficient to evaluate the potentiality in application of a magnetic refrigerant material solely by the large magnetic entropy change (ΔS_M). Besides, one of the most important parameters is the refrigerant capacity (RC), the parameter that is a measure of how much heat can be transferred between the cold and the hot sinks in one ideal refrigeration cycle, which depends on not only the ΔS_M value but also the width of ΔS_M–T curve. We have estimated the RC of DyCuSi by using the approach suggested by Gschneidner et al. [22]. The refrigerant capacity is defined as $RC = \int_{T_1}^{T_2} |\Delta S_M| \, dT$, where T_1 and T_2 are the temperatures corresponding to both sides of the half-maximum value of $-\Delta S_M$ peak, respectively. Calculations show that the maximal value of RC for DyCuSi is 381 J/kg for a magnetic field change of 0–5 T, which is larger than those for $ErRu_2Si_2$ (355 J/kg) [13], ErNiAl (246 J/kg) [19], and $DyNi_2$ (349 J/kg) [21], where the RC values are estimated from the temperature dependence of ΔS_M in the literature, respectively.

4. Conclusions

The dependences of magnetization on both magnetic field and temperature are studied for DyCuSi in detail. It is found that DyCuSi possesses a field-induced metamagnetic transition from AFM to FM states below T_N. Its critical magnetic field in metamagnetic transition increases monotonically with the decrease of temperature and reaches a value of 0.45 T at 2 K. A giant MCE without hysteresis loss around T_N is found to result from the field-induced metamagnetic transition. The maximal $-\Delta S_M$ and RC value is 24.0 J/kg K and 381 J/kg for a field change of 0–5 T, respectively. The excellent magnetocaloric properties indicate the applicability of DyCuSi to the magnetic refrigeration in the low temperature regime.

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