Large reversible magnetocaloric effect in DyCuAl compound

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Large reversible magnetocaloric effect, which is associated with a second-order magnetic transition at 28 K, has been observed in DyCuAl compound. The maximum values of magnetic entropy change $-\Delta S_M$ and adiabatic temperature change ΔT_{ad} are 20.4 J kg^{-1} K^{-1} and 7.7 K for a field change of 0–5 T, respectively. Especially, the large values of $-\Delta S_M$ (10.9 J kg^{-1} K^{-1}) and ΔT_{ad} (3.6 K) with a considerable refrigerant capacity value of 150 J kg^{-1} are also obtained for a relatively low field change of 0–2 T, suggesting that DyCuAl compound could be considered as a good candidate for low-temperature magnetic refrigerant. © *2009 American Institute of Physics*.
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I. INTRODUCTION

Magnetic refrigeration based on magnetocaloric effect (MCE) of solid-state working substances has attracted tremendous attention in recent years due to its energy-efficient and environment-friendly features as compared with the common gas-compression refrigeration technology that is used currently.[1–3] The MCE is characterized by the isothermal magnetic entropy change $(-\Delta S_M)$ or the adiabatic temperature change (ΔT_{ad}) arising from the application of a magnetic field to or the removal of a field from a system with magnetic degrees of freedom. Until now, the MCE has been applied only to magnetic refrigeration devices in a low temperature range ($T<20$ K) by using the paramagnetic salt $Gd_3Gd_5O_{12}$, $GdLiF_4$, or GdF_3.[4,5] Never has a technology of magnetic refrigeration been commercially employed in a temperature region between 20 K and room temperature. Furthermore, it is known that materials exhibiting a large MCE at temperatures below 70 K are potential magnetic refrigerants for the gas liquefiers.[3,6] Therefore, from the point of view of application, it is desirable to explore magnetocaloric materials applicable in a low temperature range.

Usually, the magnetic materials are required to possess large enough spontaneous magnetization and strong temperature dependence of magnetization around its phase transition temperature to obtain a large MCE. This is the reason why research on magnetic refrigeration is concentrated almost exclusively on rare earth compounds and crystalline materials possessing the first-order phase transition.[7–11] Unfortunately, the first-order phase transition is usually accompanied by considerable thermal and magnetic hystereses, thereby reducing the refrigerant capacity (RC) of magnetic refrigerant materials.[11,12] On the other hand, the kinetics of the first-order transformation may be so slow that it can limit the operation cycle frequency of refrigerator, thus reducing its thermal productivity. Recently, much more attention has been paid to searching for advanced magnetic refrigerant materials with a large reversible magnetic entropy change based on a second-order phase transition.[13,14] It has been reported that the RCuAl (R=rare earth) compounds with a hexagonal ZrNiAl-type structure exhibit interesting physical properties,[15–20] and their structure, phase transition, and magnetic properties have been studied in detail by neutron diffraction, specific heat, and magnetic measurements. However, a study on their magnetocaloric properties is still lacking and remains to be carried out. We have studied the magnetic properties and magnetocaloric effects of GdCuAl compounds already.[21] In the present paper, we report on a large reversible magnetic entropy change and a high RC in DyCuAl compound, which result from a second-order magnetic transition. The maximum values of $-\Delta S_M$ and ΔT_{ad} are found to be 20.4 J kg^{-1} K^{-1} and 7.7 K at ~30 K for a magnetic field change of 0–5 T, respectively.

II. EXPERIMENT

The DyCuAl ingot was prepared by arc melting Al, with a purity of 99.99 wt %, and Dy and Cu, with a purity of 99.9 wt %, in a high-purity argon atmosphere and then melt-spun into ribbons by using a single-roller melt-spinner at a cooper wheel surface speed of 50 m/s. A postannealing of the products at 873 K for 100 h and a subsequent quenching to room temperature were performed to obtain crystalline samples. X-ray powder diffraction indicates that such annealed ribbons are of single phase with a hexagonal ZrNiAl-type structure (space group $P\bar{6}2m$). The lattice parameters a and c were determined to be 7.010 and 4.020 Å, respectively, consistent with those given in Ref. 17. Magnetizations were measured as functions of temperature and magnetic field by using a superconducting quantum interference device magnetometer. Heat capacity was measured by using a physical property measurement system (Quantum Design).

III. RESULTS AND DISCUSSION

Figure 1(a) shows the temperature dependences of zero-field-cooling (ZFC) and field-cooling (FC) magnetization (M) for the DyCuAl compound under a magnetic field of 0.05 T. The DyCuAl compound exhibits a ferromagnetic-paramagnetic transition in the M-T curves, and its Curie temperature T_C, corresponding to the maximum slope of M-T

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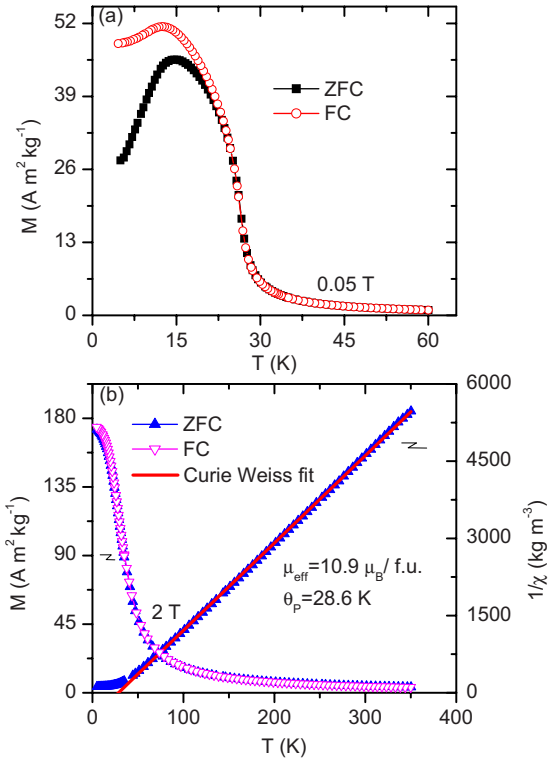

FIG. 1. (Color online) (a) Temperature dependences of ZFC and FC magnetizations under 0.05 T. (b) Temperature dependences of ZFC and FC magnetizations and the temperature variation of the ZFC inverse susceptibility fitted to the Curie–Weiss law under 2 T.

curve, is determined to be 28 K, which is in agreement with the result reported by Javorsky *et al.*[17] It can be seen from Fig. 1 that the ZFC and FC curves for DyCuAl are completely reversible around T_C as shown usually in magnetic materials with a second-order magnetic transition. However, a significant thermal irreversibility between the ZFC and FC branches is clearly observed below T_C. This irreversibility may be attributed to the domain-wall pinning effect.[22] According to powder neutron diffraction investigation,[19,20] DyCuAl undergoes only a magnetic transition from the ferromagnetic to the paramagnetic states at T_C. Therefore, the maximum value of the magnetization at low temperature (about 12 K) corresponds probably to a spin reorientation transition. In fact, it has been verified by the neutron diffraction investigation[20] that DyCuAl compound shows a uniaxial magnetic anisotropy at 1.6 K. It is possible that the easy magnetization direction of DyCuAl deviates from the *c*-axis or changes from *c*-axis to basal plane with the increase in temperature. Figure 2 shows the magnetic hysteresis loops at 5 and 20 K for DyCuAl. A large coercive field of 0.76 kOe at 5 K further reveals the easy *c*-axis magnetic anisotropy for the DyCuAl compound. However, a soft hysteresis loop with a small coercive field of 0.07 kOe is observed at 20 K, which is due to the increase in temperature and may also reflect a change of easy magnetization direction.

Figure 1(b) displays the temperature dependences of the magnetization and the reciprocal magnetic susceptibility χ_m^{-1} for DyCuAl under a field of 2 T, respectively. The susceptibility above 45 K obeys the Curie–Weiss law with an effective moment μ_{eff}=10.9 μ_B per Dy atom and a paramagnetic

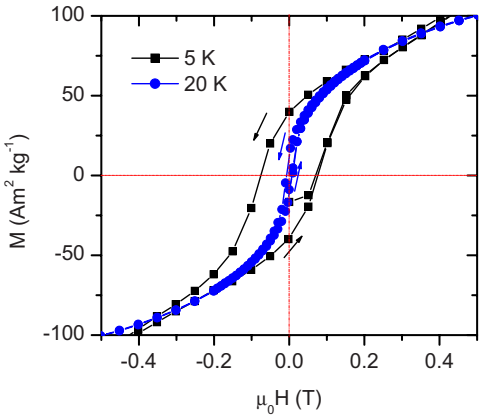

FIG. 2. (Color online) Magnetic hysteresis loops at 5 and 20 K in low magnetic fields for DyCuAl compound.

Cure temperature θ_P=28.6 K. These values consist with the results in the literature.[15] It is found that the value of μ_{eff} for DyCuAl is larger than the free-ion value for Dy^{3+} ion (10.6 μ_B), which may be attributed to the polarization of the conduction band as observed in isostructural *R*NiAl compounds.[22,23]

Figure 3(a) shows the isothermal magnetization curves for DyCuAl in a temperature range from 20 to 47 K around T_C. It is observed that each of *M*-*H* isotherms in the vicinity of T_C shows a completely reversible behavior during the field increasing and decreasing, i.e., no magnetic hysteresis

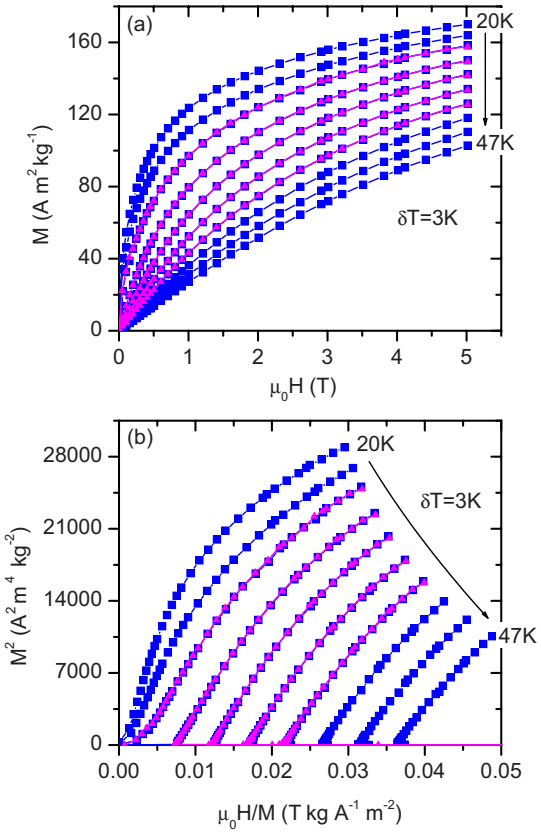

FIG. 3. (Color online) Magnetic isothermals (a) and Arrott-plots (b) of DyCuAl compound in a temperature range of 20–47 K measured during field increasing (solid squares) and decreasing (solid triangles) in temperature steps of 3 K.

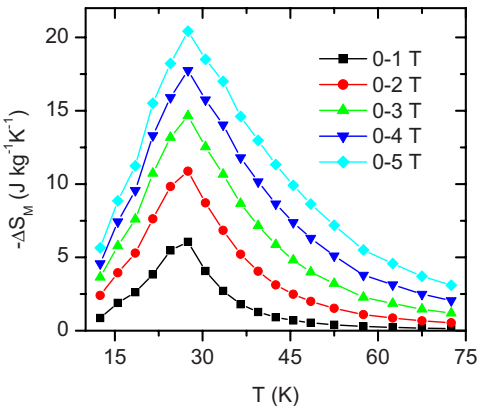

FIG. 4. (Color online) Magnetic entropy change as a function of temperature for DyCuAl compound for magnetic field changes of 0–1, 0–2, 0–3, 0–4, and 0–5 T.

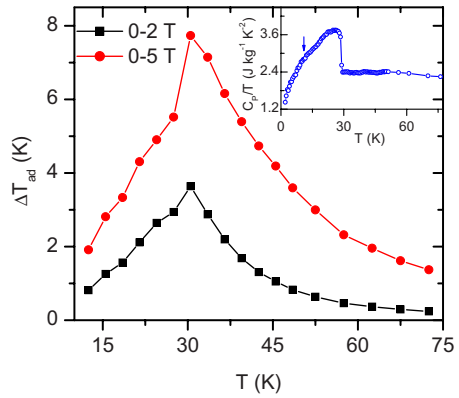

FIG. 5. (Color online) Adiabatic temperature change as a function of temperature for field changes of 0–2 and 0–5 T for DyCuAl compound. Inset plot shows the temperature dependence of zero-field specific heat.

around T_C is observed. The Arrott plot of the DyCuAl compound is shown in Fig. 3(b). According to the Banerjee criterion,[24] a magnetic transition is expected to be of the first order when the slope of M^2 versus H/M plot is negative, whereas it will be of the second order when the slope is positive. It is very clear that the Arrott plot for DyCuAl indicates a characteristic of second-order magnetic transition. The magnetic entropy change ΔS_M for DyCuAl is calculated from isothermal magnetization data by using the Maxwell relation $\Delta S_M = \int_0^H (\partial M/\partial T)_H dH$. The values of ΔS_M for different magnetic field changes as a function of temperature are shown in Fig. 4. It is observed that the temperature dependence of ΔS_M shows a maximum value around T_C. The maximum value of ΔS_M is found to increase monotonically with applied magnetic field increasing and reaches a value of 20.4 J kg^{-1} K^{-1} for a magnetic field change from 0 to 5 T, which is comparable with or much larger than those of some magnetocaloric materials with a second-order magnetic transition in a similar temperature range under the same field change, such as DyNiAl (19.0 J kg^{-1} K^{-1}),[22] $TbCoC_2$ (15.3 J kg^{-1} K^{-1}),[14] DyCoAl (16.3 J kg^{-1} K^{-1}),[25] (Er,Gd-)NiAl (10–22 J kg^{-1} K^{-1}),[26] and MnSi (3.6 J kg^{-1} K^{-1}).[27] It is interesting to note that a large reversible magnetic entropy change for DyCuAl is as high as 10.9 J kg^{-1} K^{-1} for a field change of 0–2 T, which is beneficial to the practical applications because a magnetic field of 2 T can be supplied by a permanent magnet.

In order to get a better comparison of the application potential of this compound, we have also calculated the MCE in terms of adiabatic temperature change ΔT_{ad} by using $\Delta T_{ad} = -\Delta S_M(T_0, H) \times T_0 / C_P(T_0, H_0)$, where $C_P(T_0, H_0)$ is zero-field specific heat. A broad cusp at ~12 K is also observed in the zero-field specific heat curve (see the inset of Fig. 5), which is in accord with the result of M-T curve. Figure 5 shows the temperature dependences of ΔT_{ad} of the DyCuAl compound for field changes of 0–2 and 0–5 T, and its maximum values of ΔT_{ad} are found to be 3.6 and 7.7 K, respectively. It has been reported that for magnetic field changes of 0–2 and 0–5 T, the maximum values of ΔT_{ad} are 3.5 and 7.0 K for DyNiAl (Ref. 22) and 2.6 and 4.4 K for MnSi,[27] respectively. For the (Er,Gd)NiAl compounds,[26] the maximum values of ΔT_{ad} vary in the range of 4–7 K for a field change of 0–5 T. One can find that the values of ΔT_{ad} for DyCuAl are compared well with those for some rare-earth intermetallic compounds in a similar temperature range.

RC is an important parameter that characterizes the refrigerant efficiency of the material. In the present work the value of RC for the DyCuAl compound is calculated by numerically integrating the area under the $-\Delta S_M$-T curve (Fig. 4), with the temperatures at half maximum of the peak used as the integration limits.[28] By using this method, it has been found that the RC value of the DyCuAl compound increases almost linearly with applied magnetic field and reaches a value of 423 J/kg for a field change of 0–5 T. Particularly, a high value of RC is also obtained to be 150 J kg^{-1} for a relatively low field change of 0–2 T. This attributes to the appreciably large values of ΔS_M and ΔT_{ad} obtained at T_C for DyCuAl.

IV. SUMMARY

A large reversible MCE has been observed in a DyCuAl compound with a second-order ferromagnetic-paramagnetic transition at $T_C = 28$ K. For a magnetic field change of 0–5 T, the maximum values of $-\Delta S_M$ and ΔT_{ad} of the DyCuAl compound are 20.4 J kg^{-1} K^{-1} and 7.7 K, respectively, which are comparable with or larger than those of best-known magnetocaloric materials in a similar temperature range. The maximum values of RC are found to be 150 and 423 J kg^{-1} for field changes of 0–2 and 0–5 T, respectively. The large reversible $-\Delta S_M$ and ΔT_{ad} as well as high RC indicate that DyCuAl compound could be a promising candidate for magnetic refrigeration at low temperatures.

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