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Low-temperature large magnetocaloric effect in the antiferromagnetic $ErNi_{0.6}Cu_{0.4}Al$ compound

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Magnetic properties and magnetocaloric effects (MCEs) of the $ErNi_{0.6}Cu_{0.4}Al$ compound are investigated. The compound is found to be antiferromagnet with the Néel temperature $T_N = 4$ K. An antiferromagnetic (AFM)-to-ferromagnetic (FM) transition below T_N occurs under an applied magnetic field of 0.8 kOe. The field-induced AFM-FM transition leads to a large MCE and no magnetic hysteresis loss is observed. The maximum values of magnetic entropy change (ΔS) are found to be -15.5 J/kg K and -22.5 J/kg K with a refrigerant capacity value of 122 and 354 J/kg for the field changes of 0–20 kOe and 0–50 kOe, respectively. The large ΔS as well as no hysteresis loss make $ErNi_{0.6}Cu_{0.4}Al$ an attractive candidate for low temperature magnetic refrigerant. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4775722]

I. INTRODUCTION

Magnetic refrigeration based on magnetocaloric effect (MCE) is well known because of its characteristics of high energy-efficiency and eco-friendly, especially compared with the common gas-compression refrigeration.[1–4] The MCE is characterized by the isothermal magnetic entropy change or the adiabatic temperature change arising from the application (removal) of a magnetic field to (from) a system with magnetic degree of freedom.[1–8] The feasibility of applying this technology depends highly on the design and synthesis of suitable magnetic cooling materials. Up to now, much effort such as complex heat treatments has been made to fabricate various single-phase materials with the high peak value of magnetic entropy change (ΔS),[8–10] among which the high purity Gd, $Gd_5Si_2Ge_2$, and $La(Fe,Si)_{13}$ series are the most extensively studied materials for their potential application at room temperature.[4,5] However, systems exhibiting large MCE at low temperature are also intriguing for basic research as well as special technological applications such as space science and liquefaction of hydrogen in fuel industry. The MCE has been applied to magnetic refrigeration devices to achieve millikelvin temperature by using the paramagnetic (PM) salts $Gd_3Gd_5O_{12}$, $GdLiF_4$, or GdF_3.[11,12] However, the MCE of the paramagnetic salt is small and drop off sharply with temperature increasing, and never a technology of magnetic refrigeration has been commercially employed by using rare earth-based compounds with large ΔS. Therefore, it is of great significance to explore new magnetic refrigerants with large ΔS working at low temperature.

In recent years, many investigations have focused on the rare earth-based compounds because of their large spontaneous magnetizations and strong temperature-dependent magnetizations around phase transition temperature, thereby leading to large ΔS. In the cryogenic temperature region, much effort has been devoted to the studies of the *RTX* family (R = rare-earth metal, T = transition metal, X = p-metal) or the RT_2 family.[12,13] Among the *RTX* series materials, *R*NiAl and *R*CuAl crystallize into the same hexagonal ZrNiAl-type structure.[14–17] Some rare-earth atoms in this structure form a triangular lattice as a layer. The rest of rare earth atoms and one third of T atoms are contained in a hexagonal basal plane. These two layers are separated by a nonmagnetic layer consisting of the Al element and the other T atoms.[18] The magnetic structures of this family are usually complicated at low temperature and various techniques exemplified by the neutron diffraction method and so on were employed to investigate the magnetic characteristics.[19,20] There are several reports dealing with the doping at the R site and T site. Quite a complicated combination of antiferromagnetic (AFM) and ferromagnetic (FM) states was found in several $RNi_{1-x}Cu_xAl$ compounds.[21–24] For $ErNi_{1-x}Cu_xAl$ series, the evolution of magnetism from antiferromagnetism with Er-moments within the basal plane in ErNiAl to the simple ferromagnetism with moments along the c-axis in ErCuAl is rather complex. The AFM nature with moments in the basal plane is characterized for $x \leq 0.4$. The $ErNi_{0.5}Cu_{0.5}Al$ has ferromagnetism with moments along the c-axis. For the $ErNi_{1-x}Cu_xAl$ with $x = 0.6$ and 0.8, short-range ordering was detected.[22] These magnetic phenomena can be explained by the RKKY interaction.[18,24] Though the magnetic structures of these intermetallic compounds are extensively studied, to our knowledge, their magnetocaloric properties are not yet to be investigated. In this paper, we study the magnetic properties and MCEs of $ErNi_{0.6}Cu_{0.4}Al$ compound. It is found that $ErNi_{0.6}Cu_{0.4}Al$ undergoes a field-induced AFM-to-FM transition below T_N, accompanied by a large MCE without hysteresis loss.

II. EXPERIMENTAL DETAILS

The $ErNi_{0.6}Cu_{0.4}Al$ ingot was prepared by arc melting stoichiometric Er, Cu, Ni, and Al with a purity better than

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99.9 wt. % under the protection of high-purity argon atmosphere. 2 wt. % excessive of Er component was used to compensate the weight loss in the arc melting process. The sample was turned over and re-melted four times to ensure its homogeneity. The obtained ingot was sealed in a quartz tube filled with high-purity argon before which the quartz tube had been evacuated to avoid the oxidation of the sample, annealed at 973 K for 30 days, and then quenched in liquid nitrogen. Powder X-ray diffractometer by using Cu Kα radiation was used to characterize the phase purity and crystalline structure. The magnetic measurements were carried out by using the superconducting quantum interference device magnetometer (Quantum Design). The isothermal magnetization curves were measured from low temperature to high temperature in heating process. Before measuring the next temperature, the magnetic field should be adjusted to 0 Oe to avoid the remaining magnetic field of the facility.

III. RESULTS AND DISCUSSION

Figure 1 shows the room temperature powder X-ray diffraction patterns for $ErNi_{0.6}Cu_{0.4}Al$ sample. All the peaks can be indexed and the sample is found to be of clean single phase with a hexagonal ZrNiAl-type structure (space group $P\bar{6}2m$, NO. 189). Within the experimental error, the lattice parameters a and c are determined to be 6.983 ± 0.005 and 3.820 ± 0.004 Å, respectively, consistent with the results in Ref. 22.

The zero-field cooling (ZFC) and field-cooling (FC) temperature (T)-dependences of magnetization (M) under typical fields are measured in order to determine the magnetic state, the phase transition temperature, and the nature of the transition. Figure 2(a) displays the ZFC and FC magnetization under a field of 0.1 kOe. Each of the ZFC and FC curves exhibits a peak around $T_N \sim 4$ K, which is a prominent indication of magnetic transition from AFM to PM state. The AFM nature for $ErNi_{1-x}Cu_xAl$ with Cu content $x \leq 0.4$ has been reported by neutron diffraction measurements.[22] The

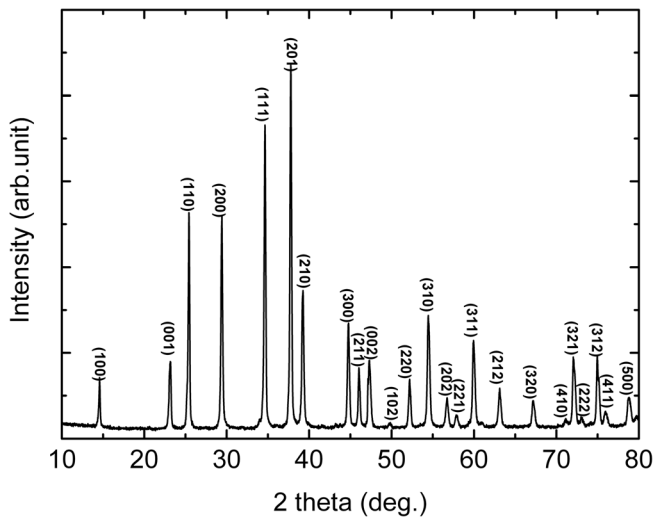

FIG. 1. XRD spectrum for the $ErNi_{0.6}Cu_{0.4}Al$ alloy.

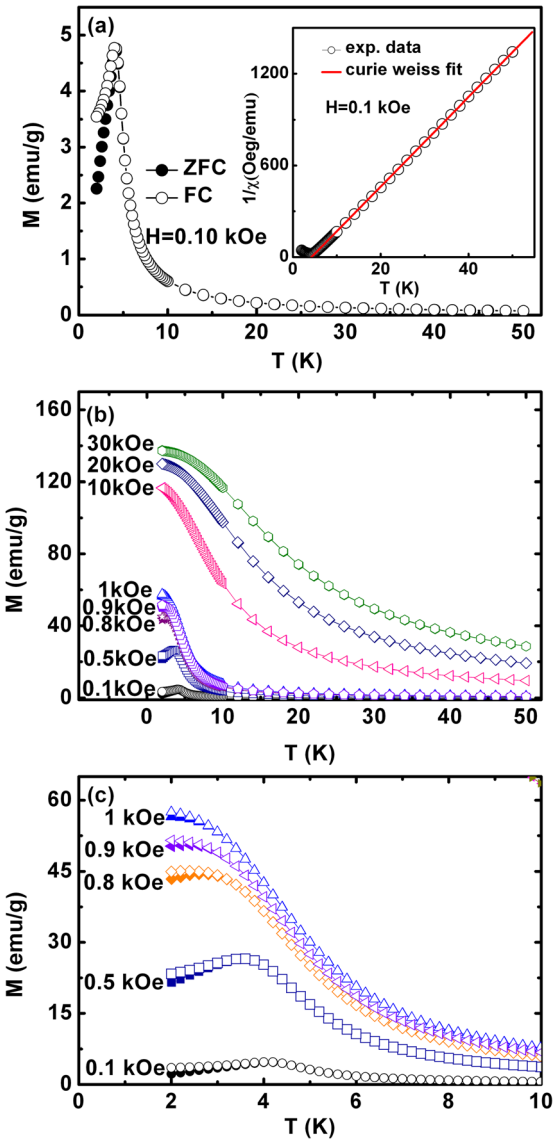

FIG. 2. Temperature dependences of magnetization measured in a field of 0.1 kOe in ZFC and FC modes for $ErNi_{0.6}Cu_{0.4}Al$ compound (a), temperature dependences of magnetization under various magnetic fields (b), and temperature dependences of magnetization under magnetic fields ranging from 0.1 kOe to 1 kOe (c). The inset of (a) displays the temperature variation of the inverse susceptibility fitted to the Curie-Weiss law.

reciprocal of the ZFC susceptibility ($1/\chi$) as a function of temperature under 0.1 kOe is plotted in the inset of Fig. 2(a). It can be seen that in the PM region, the susceptibility obeys the Curie–Weiss law. The effective magnetic moment, evaluated from the data of $1/\chi$ in the paramagnetic region, is equal to 8.31 μ_B/Er^{3+}, which is slightly smaller than the free ion value of Er^{3+} (9.59 μ_B). This discrepancy can be partly due to crystal-field effect. However, the main reason may be attributed to moment frustration arising from the competition between different exchange interaction mechanisms responsible for magnetic ordering in this kind of compound.[11] This explanation needs to be verified in the future. Figure 2(b) shows the curves of ZFC and FC magnetization versus temperature in various magnetic fields up to 30 kOe. A magnified M-T curve in low temperature range under the fields up

to 1 kOe is displayed in Fig. 2(c). There exist peaks for the present magnetization data collected at fields lower than 0.8 kOe and the magnetization decreases with temperature decreasing below the temperature at the peak position, which is in consistent with AFM nature. It should be noted that the magnetization collected at 0.8 kOe and 0.9 kOe keep almost constant with temperature decreasing to below T_N. The FC magnetic moments measured at 1 kOe and the other higher magnetic fields increase with the temperature decreasing, which corresponds to the FM ordering feature. That is, this compound undergoes a field-induced AFM-FM transition in the low temperature range under a magnetic field around 0.8 kOe. Moreover, FM-to-PM instead of AFM-to-PM transition is observed in the fields higher than 0.8 kOe. In addition, a significant thermal irreversibility between the ZFC and FC branches at low temperature is clearly observed in an applied field of up to 1 kOe. It was generally thought that the thermo-magnetic irreversibility could be observed in a narrow-domain wall pinning system and/or a frustrated system.[22–24] The $ErNi_{0.6}Cu_{0.4}Al$ is a geometrically frustrated system with large anisotropy.[22,24] The ZFC-FC difference disappears in high fields, which may result from the weakening or vanishing of magnetic frustration induced by the sufficient energy provided by the magnetic field.

Figure 3(a) displays the magnetic hysteresis loop at 2 K and the curve shows a negligible hysteresis effect, which is very favorable for the actual application of magnetic refrigerant. The inset of Fig. 3(a) shows the magnified hysteresis loop at 2 K, in magnetic field up to 2.7 kOe. We can find that there exists an obvious change in the slope of the curve in a field of 0.8 kOe, which confirms a phase transition under this magnetic field. Figure 3(b) exhibits the field dependence of magnetization in a temperature range from 2 to 6 K with an increment of 1 K, in magnetic fields ranging from 0 to 2.5 kOe. It can be seen that there exist intersections among the curves. Carefully examining the curves, one can see that the magnetization values at 3 K and 4 K are even higher than those at 2 K below a critical field of 0.9 kOe and 0.7 kOe, respectively. On the contrary, in higher fields, this condition reverses and the low-temperature magnetization becomes larger than the high-temperature value. This ensures that the compound is antiferromagnetic below T_N.[25] On the other hand, the magnetization curves are gradually saturated under high magnetic fields, that is to say, the sample can change to FM phase by applying an appropriate field (about 0.8 kOe) in our case. Such a transition has been really observed in Figs. 2(b) and 2(c) and the critical transition field coincides, indeed, with the result observed in Fig. 2. The inset of Fig. 3(b) particularizes the derivative of initial magnetic curve at 2 K in magnetic field up to 2 kOe and the result indicates a peak at 0.8 kOe, which is a distinguishing feature of phase transition.

The isothermal magnetization curves each as a function of magnetic field for $ErNi_{0.6}Cu_{0.4}Al$ compound are measured in applied fields up to 70 kOe, in a wide temperature range from 2 K to 50 K in heating mode as shown in Fig. 4(a). It should be noticed that the magnetic moments are not saturated even in a field of 70 kOe, which may be due to the AFM ground state and the frustrated structure of the sample.

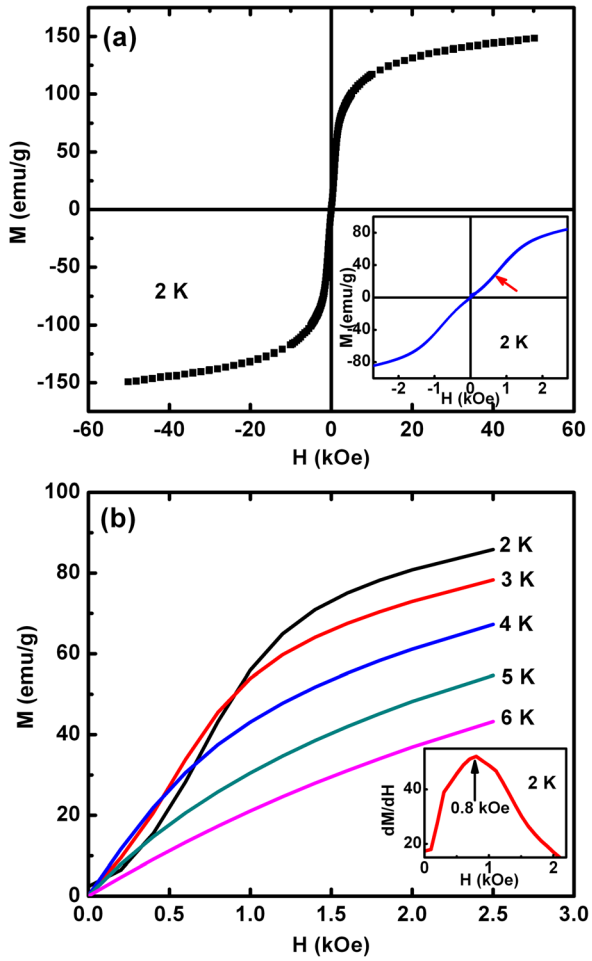

FIG. 3. Magnetic hysteresis loop at 2 K up to 50 kOe, with the inset showing the enlarged part of magnetic hysteresis loop (a) and initial isothermal magnetization curve at typical temperatures with the inset indicating the $dM/dH - H$ curve at 2 K (b).

The negative slope of the Arrott plot below T_N, which is shown in Fig. 4(b) and the inset, further confirms the occurrence of an AFM-to-FM transition.[26]

The MCE in terms of isothermal magnetic entropy change is determined from the magnetization isotherms around the transition temperature, by utilizing Maxwell's relationship $\Delta S = \int_0^H (\partial M/\partial T)_H dH$. The temperature dependences of ΔS for different magnetic field changes are shown in Fig. 5. The ΔS peak position shifts toward higher temperature and the maximum value of ΔS ascends with the field change increasing. The maximum values of ΔS are -22.5 and -27.1 J/kg K for the field changes of 0–50 and 0–70 kOe, respectively. It is evident that the peak value of ΔS is as large as those of $Gd_5(Si_2Ge_2)$ and $La(Fe,Si)_{13}$ irrespective of their transition temperatures and comparable to those of the most potential magnetic refrigerant materials in low temperature under the same field change (0–50 kOe) such as HoNiAl (-23.6 J/kg K),[27] DyNiAl (-19.0 J/kg K),[16] and DyCoAl (-16.3 J/kg K).[28] It is worthwhile to particularly note that a giant ΔS value of -15.5 J/kg K is achieved for a low field change of 0–20 kOe, which is of advantage for application.

Apart from the magnitude of the ΔS, another important parameter used to characterize the refrigerant efficiency of

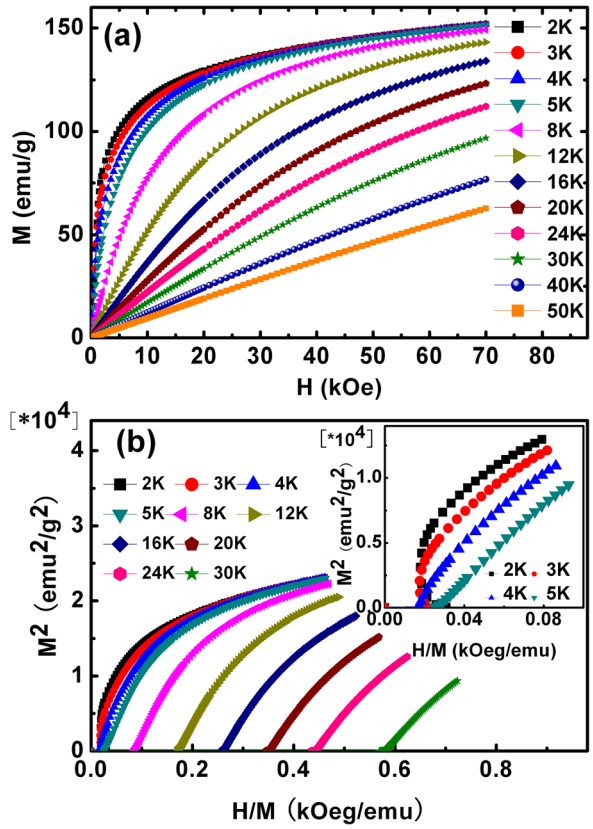

FIG. 4. Magnetic isothermals (a) and Arrott-plots (b) of $ErNi_{0.6}Cu_{0.4}Al$ compound measured during field increasing. The inset of (b) displays the Arrott plots at temperatures of 2 K, 3 K, 4 K, and 5 K, respectively.

the material is the refrigerant capacity (RC). The value of RC for the $ErNi_{0.6}Cu_{0.4}Al$ compound is calculated by numerically integrating the area under the ΔS versus T plot (Fig. 5), with the temperatures at half maximum of the peak used as the integration limits. One can find that the RC value of the $ErNi_{0.6}Cu_{0.4}Al$ increases with the field increasing. The RC values reach 354 and 502 J/kg for the field changes of 0–50 kOe and 0–70 kOe, respectively. The close attention should be paid to that a high value of RC is also obtained to be 122 J/kg with the peak value of ΔS at 5.5 K for a relatively low field change of 0–20 kOe, which can be provided by the permanent magnet. Regarding the low transition temperature, this merit makes $ErNi_{0.6}Cu_{0.4}Al$ an alternative material for the refrigeration application below 10 K.

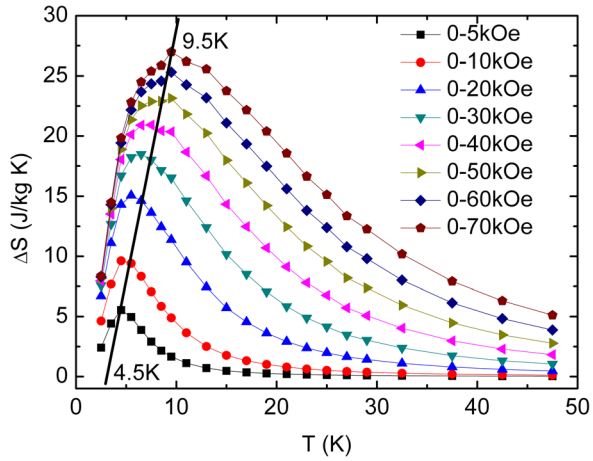

FIG. 5. Magnetic entropy changes each as a function of temperature for $ErNi_{0.6}Cu_{0.4}Al$ compound for magnetic field changes of 0–5 kOe, 0–10 kOe, 0–20 kOe, 0–30 kOe, 0–40 kOe, 0–50 kOe, 0–60 kOe, and 0–70 kOe.

IV. CONCLUSIONS

The magnetic properties and the MCEs of $ErNi_{0.6}Cu_{0.4}Al$ are studied. The characterization of this sample by magnetization measurements reveals the AFM ground state. The $ErNi_{0.6}Cu_{0.4}Al$ undergoes a field-induced AFM-FM transition below $T_N \sim 4$ K under a field of 0.8 kOe. The existence of thermomagnetic irreversibility under low field is attributed to the frustrated effect and large anisotropy. Large values of reversible ΔS with maxima of -15.5 J/kg K and -22.5 J/kg K are obtained for the field changes of 0–20 kOe and 0–50 kOe, respectively. The RC value of the $ErNi_{0.6}Cu_{0.4}Al$ increases with the field increasing and reach 122 and 354 J/kg for field changes of 0–20 kOe and 0–50 kOe, respectively. Furthermore, $ErNi_{0.6}Cu_{0.4}Al$ is magnetically soft that can reduce the energy loss during the cooling cycles which is an additional criterion for a good refrigerant material. The large MCE, relatively high RC, and the magnetic softness jointly make the present compound a promising candidate for magnetic refrigerant in the low temperature range ($<$10 K).

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