AIP | Journal of Applied Physics

Low-temperature reversible giant magnetocaloric effect in the HoCuAl compound

L. C. Wang, Q. Y. Dong, Z. J. Mo, Z. Y. Xu, F. X. Hu et al.

Citation: J. Appl. Phys. **114**, 163915 (2013); doi: 10.1063/1.4826270
View online: http://dx.doi.org/10.1063/1.4826270
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v114/i16
Published by the AIP Publishing LLC.

Low-temperature reversible giant magnetocaloric effect in the HoCuAl compound

L. C. Wang,[1] Q. Y. Dong,[2] Z. J. Mo,[3] Z. Y. Xu,[1] F. X. Hu,[1] J. R. Sun,[1] and B. G. Shen[1,a)]
[1]*State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China*
[2]*Department of Physics, Capital Normal University, Beijing 100048, China*
[3]*School of material Science and Engineering, Hebei University of Technology, Tianjin 300401, China*

(Received 31 August 2013; accepted 4 October 2013; published online 31 October 2013)

Magnetic properties and magnetocaloric effect (MCE) of the HoCuAl compound is investigated. The compound is found to be ferromagnetic and undergoes a second-order phase transition from ferromagnetic (FM)-to-paramagnetic (PM) state around Curie temperature $T_C = 11.2$ K. A giant MCE is observed and no magnetic hysteresis loss is found. The maximum values of magnetic entropy change (ΔS) are found to be -17.5 J/kg K and -30.6 J/kg K with a refrigerant capacity (RC) value of 178 and 486 J/kg for the field changes of 0–20 kOe and 0–50 kOe, respectively. The large ΔS as well as no hysteresis loss imply HoCuAl a promising candidate for low temperature magnetic refrigerant. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4826270]

I. INTRODUCTION

In recent years, magnetocaloric effect (MCE) technology has become a challenge to the conventional gas compression refrigeration that with the main shortcomings of low efficiency and environmental contamination.[1–7] Exploration of effective MCE materials and their application as magnetic refrigerants have stirred up so much enthusiasm in the scientific community.[1–11] Since the discovery of $Gd_5Si_2Ge_2$ that with Curie temperature (T_C) near room temperature and a field induced first-order magnetic and structural transitions, the following research work mainly consists of looking for materials with first-order magnetic transition (FOMT) that is expected to possess large magnetic entropy change (ΔS), in which such as $Gd_5Si_2Ge_2$,[1] $La(Fe_{1-x}Si_x)_{13}$,[2,3] $MnFeP_{1-x}As_x$,[4] and $MnAs_{1-x}Sb_x$,[5] are the most extensively studied materials working at room temperature. However, the serious defects for FOMT materials are the narrow working temperature region, apparent magnetic anisotropy, and larger hysteresis, which may greatly reduce the MCE and the relative refrigerant capacity (RC). Companied with the crisp mechanical character of the rear earth transition metal intermetallic compounds and the Mn-based alloys, no magnetic refrigerants employing these materials have been commercially used until now. On the other hand, relevant studies on the magnetic refrigerant materials worked in low temperatures range ($<$20 K) also received renewed attentions for basic research as well as special technological application demand such as space science and liquefaction of hydrogen that is needed for its storage and transportation.[6,8] Up to now, paramagnetic (PM) salts and garnets are the only two kinds of materials that have been commercially applied to magnetic refrigeration devices in ultra-low temperature range.[12,13] However, the MCE of the PM salts are minimal and attenuate sharply with temperature increasing and never has a technology of magnetic refrigeration 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 most cases, ΔS, adiabatic temperature change (ΔT_{ad}) and RC are the three most important parameters used to quantify the MCE character of the materials.[1–4] Recently, plenty of rare earth (R)-3d transition metal intermetallic compounds with large MCE in low temperature range have been reported, in which *R*NiAl and *R*CuAl belong to the *RTX* family (R = rare-earth metal, T = transition metal, X = p-metal), and crystallize in the same hexagonal ZrNiAl-type structure.[14–17] On aggregate, ferromagnetic (FM) order were found in *R*CuAl alloys, while antiferromagnetic (AFM) order found in the *R*NiAl ones.[18–22] The magnetic structure and the magnetism of these materials originate in the magnetic moment of R ions. The Ni/Cu and Al atoms are non-magnetic. All the R atoms occupy 3*g* sites while all Al atoms occupy 3*f* sites. Cu atoms occupy two non-equivalent 1*b* and 2*c* positions.[23] The basal plane layer formed by all the R atoms and one-third of Cu atoms and the other non-magnetic layer made up by all the Al atoms and two-thirds of Cu atoms distributed alternately along the *c*-axis. It can be expected that the stack structure of the layers may lead to large magnetocrystalline anisotropy. In recent years, there are some works focusing on the doping at the *R* site and the *T* site, and MCE were extensively probed in *R*NiAl and *R*CuAl compounds as potential magnetic refrigerants working in low temperature. Dong *et al.* have reported the magnetic properties and the MCE for the ErCuAl and HoCuAl melt-spun ribbons but there exists some impurity phase in the HoCuAl ingot.[23] In this paper, we synthesized polycrystalline HoCuAl intermetallic compound of high purity and investigated its magnetic properties and the MCE property. The maximum values of ΔS are found to be -17.5 J/kg K and -30.6 J/kg K with RC value of 178 and 486 J/kg without hysteresis loss, for the field changes of 0–20 kOe and

a)Author to whom correspondence should be addressed. Electronic mail: shenbg@aphy.iphy.ac.cn.

0–50 kOe, respectively. The excellent MCE performance of HoCuAl makes it a fascinating candidate refrigerant material in low temperature.

II. EXPERIMENTAL DETAILS

The polycrystalline HoCuAl ingot was prepared by arc melting Ho, Cu, and Al with a purity better than 99.9 at. % in stoichiometric proportion under the protection of high-purity argon atmosphere. 3 at. % excessive of Ho component was added to compensate the weight loss due to the volatility in the arc melting process. The sample was turned upside down and re-melted for four times to ensure its homogeneity. The as-cast ingot was annealed in a quartz tube filled with high-purity argon at 973 K for 2 months and then quenched into liquid nitrogen. Powder X-ray diffraction (XRD) was adopted to characterize the phase purity and crystalline structure by using Cu Kα radiation from Broker Inc. The magnetization as a function of T and magnetic field were carried out by using the superconducting quantum interference device magnetometer (MPMS, Quantum Design). The isothermal magnetization curves were collected in a heating process from low temperature to high temperature. Before measuring the next temperature, the magnetic field should be oscillated to 0 Oe for avoiding the remaining magnetic field of the facility. The AC magnetic measurement was performed in wide frequency range by employing the physical properties measurement system (PPMS, Quantum Design).

III. RESULTS AND DISCUSSION

The XRD patterns with clean background for HoCuAl, as shown in Figure 1, can be indexed to a single hexagonal ZrNiAl-type structure (space group $P\bar{6}2m$, NO. 189). For synthesizing this sample, we prepared a series of samples with excessive Ho of 1% to 5% with increment of 1%. Different with the other samples with impurity phase, sample with excess Ho of 3% was the only sample with clean phase. Impurity phase was also detected in Ref. 23 in which 5% excess of Ho were added. It can be concluded that the excessive amount of Ho is of significant importance to the quality of the sample. The lattice parameters a and c are determined to be 6.9969 ± 0.0004 and 4.0157 ± 0.0002 Å, respectively, consistent with the published papers.[15,24]

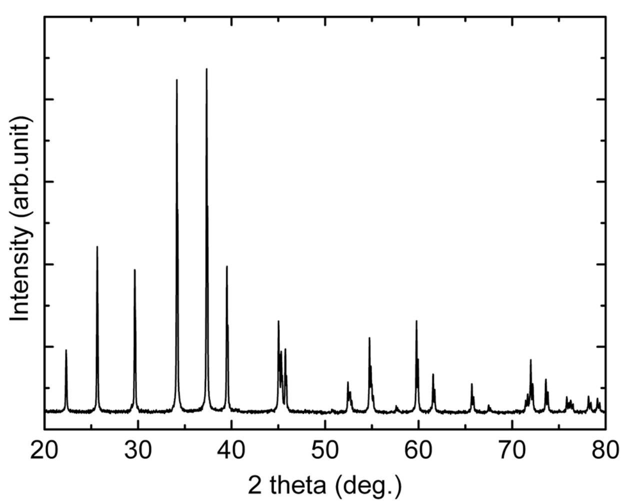

FIG. 1. XRD spectrum for the HoCuAl alloy.

To explore the magnetic ground state, the phase transition temperature, and the nature of the transition of HoCuAl, the magnetization as a function of temperature (*M-T*) for HoCuAl at the zero-field cooled (ZFC) case and field cooled (FC) case was measured with a magnetic field of 0.1 kOe, and the results are displayed in Figure 2(a). A FM to PM transition occurred around $T_C = 11.2$ K, as determined by the minimum of dM/dT. Within the experimental error, T_C consistent with the results in earlier reports.[15,24] The reciprocal of dc susceptibility ($1/\chi$) as a function of temperature under 0.1 kOe and the Curie-Weiss fit is plotted in the inset of Fig. 2(a). The susceptibility in the PM region obeys the Curie–Weiss law with the paramagnetic Curie temperature $\theta_p = 10$ K that confirms the FM ground state of the sample. The effective magnetic moment μ_{eff} deduced from the fitting curve is equal to $9.6\mu_B$, which is slightly smaller than the free ion value of Ho^{3+} ($10.6\mu_B$). This difference can be partly due to crystal-field effect and this explanation needs to be verified in the future. Furthermore, it is clearly seen from Fig. 2(a) that the ZFC and FC curves around T_C are completely reversible as usually observed in second order magnetic transition (SOMT), but a significant thermal

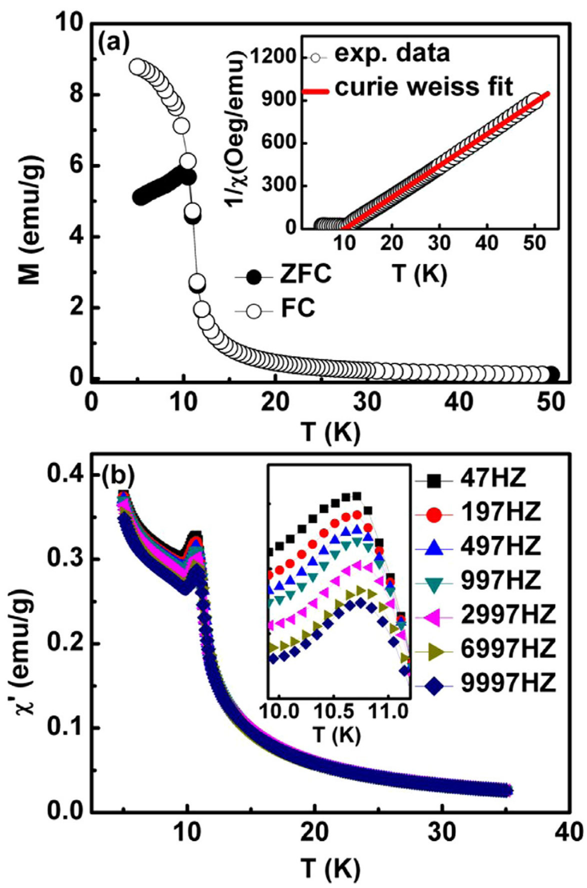

FIG. 2. (a) Temperature dependences of magnetization measured in ZFC and FC cases for HoCuAl compound under a magnetic field of 0.1 kOe. The inset shows the temperature variation of corresponding inverse dc susceptibility fitted to the Curie-Weiss law. (b) The first order (real part) ac susceptibilities of HoCuAl collected at various frequencies without dc field.

discrepancy between ZFC and FC branches emerges below T_C. This thermo-magnetic irreversibility can be observed in many cases, such as narrow-domain wall pinning systems, materials with competing magnetic interactions and ferromagnetic materials with high anisotropy.[22,25,26] Aiming at investigating the origin of this irreversibility, the ac magnetic susceptibilities of HoCuAl have been collected in frequencies verified from 47 to 9997 Hz and are shown in Figure 2(b). The enlarged part of the peak position is plotted in the inset of Fig. 2(b). It is found that the peak position of χ' does not show an obvious dependence on frequency, suggesting that the irreversibility is not related to the glass system with competing magnetic interactions.[26] On the other hand, except for the layer structure of the crystalline that may lead to anisotropy, neutron diffraction investigations also determined that RCuAl (R = Er, Tb, Dy) compounds exhibit a collinear ferromagnetic structure with magnetic moments of R ions aligned along the *c* axis, indicating the strong uniaxial anisotropy of this sample.[21] It has been reported that the domain wall width could be comparable to that of lattice spacing in RNi_2Mn compound with high anisotropy and low ordering temperature, thus leading to a large pinning effect.[25] Taking into account of the magnetic anisotropy and low T_C for HoCuAl, the thermo-magnetic irreversibility may attribute to the narrow domain wall pinning effect. The domain walls are pinned in ZFC condition for the reason that the thermal energy is not so strong enough that can overcome the energy barriers. This leads to the monotonic decreasing magnetization as a function of temperature in the temperature range lower than 9.5 K. On contrary, in FC condition, the magnetic field prevents the pinning effect during the cooling process.

The magnetization isotherms as a function of magnetic field (*M-H*) for HoCuAl was measured in the vicinity of T_C in applied fields up to 50 kOe, in a wide temperature range from 5 K to 50 K in heating mode, were shown in Figure 3(a). The inset of Fig. 3(a) displays the magnetic hysteresis loop at 5 K and the curve shows a negligible hysteresis effect, which is beneficial for the actual application of magnetic refrigerant. The saturation magnetic moment is determined to be 9.15 μ_B by extrapolating $1/H$ to 0 using the *M-H* curve measured at 5 K, and this value is lower than the expected gJ value of 10.0 μ_B for a free Ho^{3+} ion. Similar phenomenon has also been observed in other RFeSi compounds, which is attributed to the quenching effect of a strong crystalline-electric-field (CEF).[27] The Arrott plots of HoCuAl were presented in Figure 4(b). The occurrence of a SOMT FM-to-PM transition was confirmed according to Banerjee's criterion.[28]

The large saturation magnetic moment as 200 emu/g and the sharp change around T_C in the *M-T* curves indicate a possible large MCE. As conveniently and successfully applied in SOPT system, the MCE partly represented by the isothermal magnetic entropy change is obtained 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 Figure 4. The maximum values of ΔS ascend monotonically with the field change increasing. The maximum

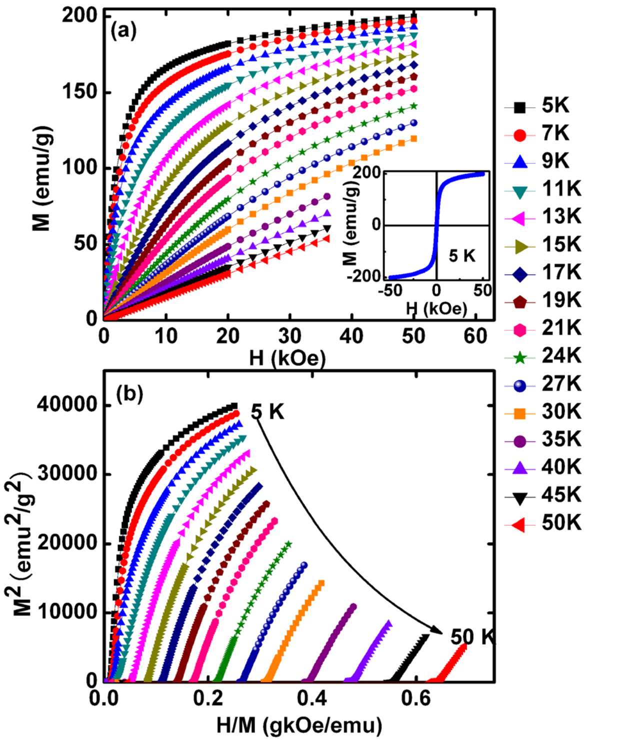

FIG. 3. (a) Magnetic isothermals and (b) Arrott-plots of HoCuAl compounds measured during field increasing. The inset of (a) displays Magnetic hysteresis loop at 5 K up to 50 kOe.

values of ΔS are equal to -17.5 J/kg K and -30.6 J/kg K for the field changes of 0–20 kOe and 0–50 kOe, respectively. In addiction, RC is determined by adopting the formula $RC = \int_{T_1}^{T_2} |\Delta S| dT$ as another important parameter to character the refrigerant efficiency of the material, in which T_1 and T_2 correspond to temperatures at both sides of half maximum of the ΔS peak. It is clearly seen that the RC values of the HoCuAl increase with the field increasing and reach 178 and 486 J/kg for the field changes of 0–20 kOe and 0–50 kOe, respectively. It is evident that the peak value of ΔS is larger than those of the most potential magnetic refrigerant materials in low temperature under the same field change (0–50 kOe) such as Er_3Ni_2 (-19.5 J/kg K)[29] and ErFeSi (-23.1 J/kg K),[8] even compared to $ErCo_2$ (31.9 J/kg K).[6] It is worthwhile to particularly note

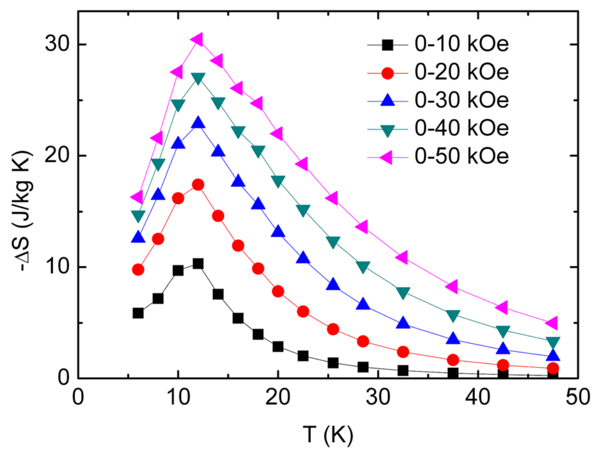

FIG. 4. Magnetic entropy changes as a function of temperature for HoCuAl compounds for various magnetic field changes.

that a giant ΔS of -17.5 J/kg K with RC value of 178 J/kg is achieved for a low field change of 0–20 kOe, which is easily provided by permanent magnet. These merits make HoCuAl an alternative material for the low temperature refrigeration application in the near future.

IV. CONCLUSIONS

In summary, HoCuAl crystallized in ZrNiAl-type structure and undergoes a second-order FM-to-PM phase transition around $T_C = 11.2$ K. The thermomagnetic irreversibility between ZFC and FC curves below T_C is attributed to narrow domain wall pinning effect. A giant reversible MCE is observed with maximum ΔS of -17.5 J/kg K and -30.6 J/kg K with corresponding RC values of 178 and 486 J/kg for the field changes of 0–20 kOe and 0–50 kOe, respectively, which is comparable or much larger than those popular MCE materials in same temperature range. The outstanding MCE performance implies HoCuAl a promising candidate for low temperature magnetic refrigeration.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (11274357, 51021061, and 51271196), the Key Research Program of the Chinese Academy of Sciences, the Hi-Tech Research and Development program of China (2011AA03A404), and the National Basic Research Program of China (2010CB833102), and is a part of the Beijing Excellent talent training support (Grant No. 2012D005016000002).

[1] V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).
[2] B. G. Shen, F. X. Hu, Q. Y. Dong, and J. R. Sun, Chin. Phys. B **22**, 017502 (2013).
[3] S. Fujieda, A. Fujita, and K. Fukamichi, Appl. Phys. Lett. **81**, 1276 (2002).
[4] O. Tegus, E. Bruck, K. H. J. Buschow, and F. R. de Boer, Nature (London) **415**, 150 (2002).
[5] H. Wada and Y. Tanabe, Appl. Phys. Lett. **79**, 3302 (2001).
[6] E. Gratz and A. S. Markosyan, J. Phys.: Condens. Matter **13**, R385 (2001).
[7] K. A. Gschneidner, Jr., V. K. Pecharsky, and A. O. Tsokol, Rep. Prog. Phys. **68**, 1479 (2005).
[8] H. Zhang, B. G. Shen, Z. Y. Xu, J. Shen, F. X. Hu, J. R. Sun, and Y. Long, Appl. Phys. Lett. **102**, 092401 (2013).
[9] D. X. Li, T. Yamamura, S. Nimori, Y. Homma, F. Honda, and D. Aoki, Appl. Phys. Lett. **102**, 152409 (2013).
[10] R. D. Shull, V. Provenzano, A. J. Shapiro, A. Fu, M. W. Lufaso, J. Karapetrova, G. Kletetschka, and V. Mikula, J. Appl. Phys. **99**, 08K908 (2006).
[11] V. Franco, J. S. Blázquez, and A. Conde, Appl. Phys. Lett. **89**, 222512 (2006).
[12] J. A. Barclay and W. A. Steyert, Cryogenics **22**, 73 (1982).
[13] W. F. Giauque and D. P. MacDougall, Phys. Rev. **43**, 768 (1933).
[14] J. Prchal, E. Šantavá, and D. Schmoranzer, Physica B **404**, 3056 (2009).
[15] A. V. Andreev, P. Javorský, and A. Lindbaum, J. Alloys Compd. **290**, 10 (1999).
[16] N. K. Singh, K. G. Suresh, R. Nirmala, A. K. Nigam, and S. K. Malik, J. Appl. Phys. **99**, 08K904 (2006).
[17] H. Takeya, V. K. Pecharsky, K. A. Gschneidner, Jr., and J. O. Moorman, Appl. Phys. Lett. **64**, 2739 (1994).
[18] J. Jarosz, E. Talik, T. Mydlarz, J. Kusz, H. Böhm, and A. Winiarski, J. Magn. Magn. Mater. **208**, 169 (2000).
[19] P. Javorský, P. Burlet, E. Ressouche, V. Sechovský, H. Michor, and G. Lapertot, Physica B **225**, 230 (1996).
[20] B. J. Korte, V. K. Pecharsky, and K. A. Gschneidner, Jr., J. Appl. Phys. **84**, 5677 (1998).
[21] J. Prchal, T. Naka, M. Míšek, O.r Isnard, and P. Javorský, J. Magn. Magn. Mater. **316**, e499 (2007).
[22] J. Prchal, P. Javorský, V. Sechovský, M. Dopita, O. Isnard, and K. Jurek, J. Magn. Magn. Mater. **283**, 34 (2004).
[23] Q. Y. Dong, J. Chen, J. Shen, J. R. Sun, and B. G. Shen, J. Magn. Magn. Mater. **324**, 2676 (2012).
[24] P. Javorský, L. Havela, V. Sechovský, H. Michor, and K. Jurek, J. Alloys Compd. **264**, 38 (1998).
[25] J. L. Wang, C. Marquina, M. R. Ibarra, and G. H. Wu, Phys. Rev. B **73**, 094436 (2006).
[26] F. Yuan, J. Du, and B. L. Shen, Appl. Phys. Lett. **101**, 032405 (2012).
[27] A. Prasad, C. Geibel, and Z. Hossain, J. Magn. Magn. Mater. **322**, 2545 (2010).
[28] S. K. Banerjee, Phys. Lett. **12**, 16 (1964).
[29] Q. Y. Dong, J. Chen, J. Shen, J. R. Sun, and B. G. Shen, Appl. Phys. Lett. **99**, 132504 (2011).