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Reversal Magnetocaloric Effect in the Antiferromagnetic $TbFe_2Al_{10}$ Compound

Ruo-Shui Liu[1], Jun Liu[1, 2], Lichen Wang[1], Xiang Yu[1], Chenhui Lv[1], Zhengrui Li[1], Yan Mi[1], Lifeng Liu[1], Shuli He[1, *]

[1]Department of Physics, Capital Normal University, Beijing, China

[2]State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing, China

Email address:

1157113729@qq.com (Ruo-Shui Liu), shulihe@cnu.edu.cn (Shuli He)

[*]Corresponding author

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Abstract: Magnetocaloric effect (MCE) technology is considered as one of the most important fundamental thermodynamic effects, and plays an important role in the refrigeration area for its high energy-efficiency and eco-friendly characteristics. Rear earth based low temperature magnetic refrigerant shows broad application prospect in the future. Low cost and high processability are so important to the application in the refrigeration machine. In this paper, pure phase $TbFe_2Al_{10}$ was prepared by arc melting and long-time annealing process. The magnetic properties and magnetocaloric effect (MCE) of the $TbFe_2Al_{10}$ compound were intensively studied. It was determined to be antiferromagnetic with the Néel temperature T_N=18 K. Two metamagnetic transitions from antiferromagnetic (AFM) to ferrimagnetic (FIM) and ferrimagnetic to ferromagnetic (FM) state occurred at 5 K under a crucial applied magnetic field of 0.95 T and 1.89 T, respectively. Field variation generated a large MCE and no magnetic hysteresis loss was observed. The maximum values of magnetic entropy change (ΔS) were found to be -4.5 J/kg K and –6.7 J/kg K for the field changes of 0-5 T and 0-7 T, respectively. The large ΔS with no hysteresis loss as well as low proportion of rare earth (Tb) in crude materials make $TbFe_2Al_{10}$ a competitive candidate as low temperature magnetic refrigerant.

Keywords: $TbFe_2Al_{10}$, Antiferromagnetic, Metamagnetic Transition, Magnetocaloric Effect

1. Introduction

Nowadays, People's awareness of environmental protection is increasing, and eco-friendly technology is finding its way in actual application. In the refrigeration area, magnetocaloric effect (MCE) technology plays an important role for its high energy-efficiency and eco-friendly characteristics, especially compared with the traditional common gas compression refrigeration. [1-9] Normally, magnetic refrigeration working materials can be cataloged into low temperature zone (below 20 K), medium temperature zone (20-77 K) and high temperature zone (77 K or above, including room temperature) magnetic refrigeration materials, according to different working temperature zones. In the past several decades, domestic and foreign scientific research teams have made a series of important progress in the exploration and design of magnetocaloric materials. [5-9] In the zone of room temperature, Professor Pecharsky and Gschneidner of the Ames Laboratory in the United States reported the $Gd_5(Si_xGe_{1-x})_4$ series of compounds with giant magnetocaloric effects in 1997. [8] In the same year, Professor Du in Nanjing University has extensively studied the perovskite-like compound $La_{1-x}Ca_xMnO_3$; [9] Consequently, Ni-Mn-Ga alloy and La (Fe, Si)$_{13}$ materials were reported. [10-11] On the other hand, $MnFeP_{1-x}As_x$ compounds were determined to be with giant magnetocaloric effect. [12] In the low temperature zone, Giauque and MacDougall firstly used $Gd_2(SO_4)_3 \cdot 8H_2O$ as the working material for the experiment of adiabatic demagnetization, and obtained the ultra-low temperature of 0.25 K. This outstanding contribution won the Nobel Prize in Chemistry in 1949. [13]

Paramagnetic salts were commercially used in large scale, but the magnetocaloric effect was small. Rare earth based low-temperature magnetocaloric materials have been

extensively studied for their rich magnetic properties, including the orthogonal structure FeB type, TiNiSi type, Fe_3C type, CrB type, Co_2Si type material, tetragonal structure CeFeSi type, Zr_3A_{l2} type and Laves phase RCo_2 (R-rare earth) materials, cubic structure NaCl type, hexagonal structure ZrNiAl type, and $MgZn_2$ type material. [14] In the field of application, Hashimoto et al. [15] designed $(ErAl_2)_{0.312}$ $(HoAl_2)_{0.198}$ $(Ho_{0.5}Dy_{0.5}A_{l2})_{0.490}$ composite and Wang et al. used electronic voltage to adjust the phase transition temperature of the material. [16] The magnitude of MCE is quantified by the isothermal magnetic entropy change or the adiabatic temperature change under the variation of the magnetic field. [7-16] Considering the low value of MCE as disadvantage of the paramagnetic salts, we select $TbFe_2Al_{10}$ with AFM in order to investigate its magnetic and MCE properties hoping for its excellent performance. It can be taken as a potential candidate refrigerant in low temperature by taking into consideration its virtues of large ΔS without hysteresis loss in terms of low transition temperature (18 K).

2. Materials and Experiments

The $TbFe_2Al_{10}$ ingot was prepared by arc melting method on a water-cooled copper crucible under protection of high-purity argon atmosphere. The starting materials (Tb, Fe and Al) were weighted with the stoichiometric amount with purity of 99.9 wt.%. Considering the weight loss during the arc melting, 2 wt.% excessive Tb was added. The oxide layers on the crude metals were abolished before weighting for better purity and the sample was threshed over and remelted for five times to ensure homogeneity. After being sealed in a quartz tube fulfilled with high-purity argon atmosphere and then annealed at 1073 K for 2 weeks, the as-obtained ingot was rapidly cooled to room temperature to obtain a single phase $TbFe_2Al_{10}$ compound. The phase and crystal structure of the sample were examined by a X-ray diffractometer (D8, Bruker Inc) using a Cu target, and the GSAS software was used to determine the lattice parameter and phase purity. The magnetic properties were characterized on a small piece of the sample by a superconducting quantum magnetron interferometer (SQUID, Quantum Design).

3. Result

Figure 1 shows the standard θ-2θ powder X-ray diffraction (XRD) patterns for $TbFe_2Al_{10}$ sample in step mode, which is collected at room temperature. The black circle pattern is the data collected by the Bruker D2 diffractometer and the red line is the calculated patterns of $TbFe_2Al_{10}$ simulated by GSAS software. The result indicates that the Bragg position and the experimental data are perfectly matched. The calculated data and experimental data are also well fitted, which proves that the sample is a pure phase orthogonal $SmFe_2Al_{10}$ (space group: *Cmcm*) type structure. The lattice parameters a, b and c are determined to be 8.969217, 10.155550 and 9.016826 Å, respectively, consistent with previous literature reports. [17-19].

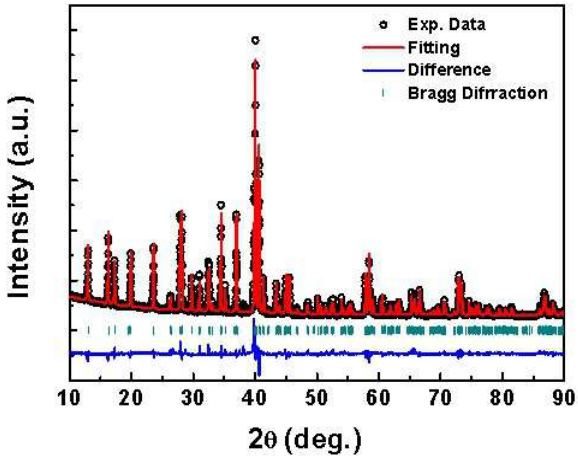

Figure 1. *XRD spectrum for the $TbFe_2Al_{10}$ alloy.*

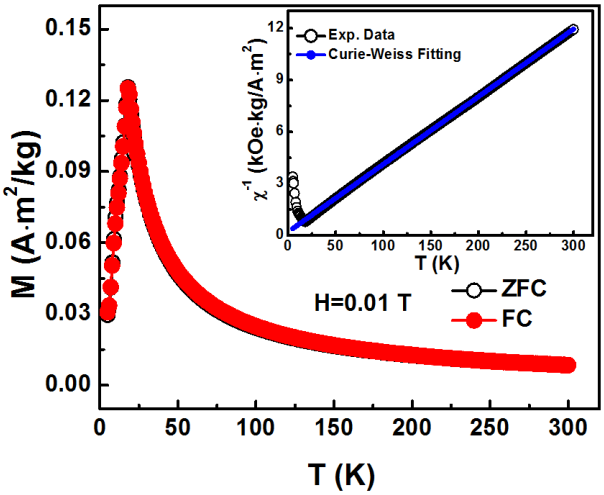

Figure 2. *Temperature dependences of magnetization measured in ZFC and FC modes for $TbFe_2Al_{10}$ compound. The inset displays the temperature variation of the inverse susceptibility fitted to the Curie-Weiss law.*

Figure 2 displays the curves of magnetization VS temperature (*M-T*) both under zero-field cooling (ZFC) and field-cooling (FC) modes. The data were collected under 0.01 T, from 5 K to 300 K. The *M-T* curves measured with a small magnetic field is generally used to determine the transition temperature and the ground state of the sample, with applied magnetic field being 0.01 T in this paper. Two peaks around 18 K emerge both in ZFC and FC curve as the temperature decrease, indicating that the magnetic ground state of the material is a typical antiferromagnetic (AFM) behavior. And the AFM ground state with Néel temperature T_N of 18 K agrees excellently with the results in the other previous works. [17-20] The dependence between reciprocal of susceptibility ($1/\chi$) and temperature is plotted in the inset of Figure 2, with the data derived from the paramagnetic zone in ZFC curve. The $1/\chi$-*T* curve is usually used for obtaining the paramagnetic Curie temperature (θp) and effective magnetic moments (μeff). It can be seen that the $1/\chi$ matches well with the Curie–Weiss law in the PM region. The θp and μeff are determined to be -5 K and 3.32

μB, respectively. The *μeff* value fits well with the free ion value of Tb^{3+} (2.54 μB) and the negative values of *θp* are always found in samples with anti-ferromagnetic ordering. [20]

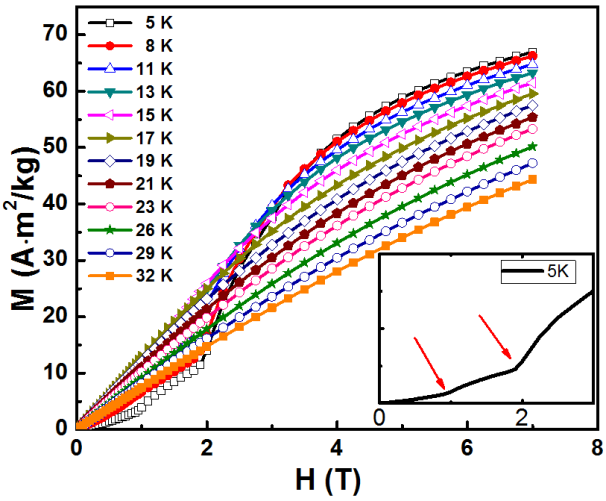

Figure 3. *M-H curve of $TbFe_2Al_{10}$ sample at 5K up to 32K, with the inset showing the enlarged part of magnetic hysteresis loop at 5K.*

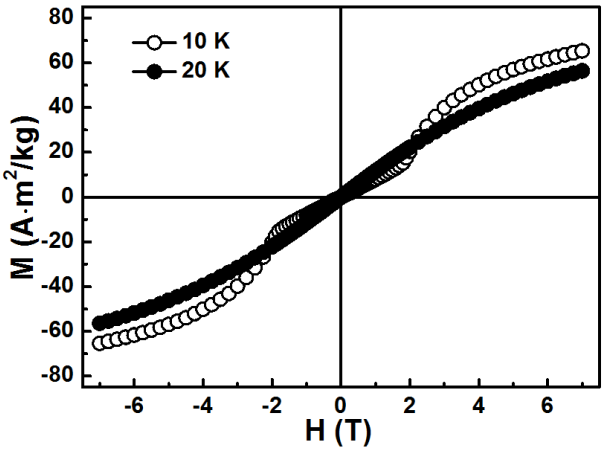

Figure 4. *M-H curve of $TbFe_2Al_{10}$ sample at specific temperature 10K and 20K.*

Figures 3 exhibits the initial magnetization curves in a temperature range of 5-32 K with magnetic fields up to 7 T. The inset shows the enlarged part of magnetization curve at 5 K. The crossover between the curves and the obvious metamagnetic behavior confirm the antiferromagnetic state at low temperatures. Two magnetic transformations occurr at 0.95 T and 1.89 T in the magnetization curve at 5 K, respectively. In the previous neutron diffraction study, Reehuis et al. indicated that the two phase transitions are antiferromagnetic-ferrimagnetic and ferrimagnetic-ferromagnetic phase transition [17]. A study by Ashish Khandelwal et al. pointed out that there was also a transition in 3 T, but did not specify the cause [18]. For the phase transition of 3 T, this paper does not do detailed research, but the complex magnetic phase transition exhibited by this material is still worthy of further investigation. We also hope to carry out research through neutron diffraction or other methods to clarify these transitions.

Figure 4 displays the magnetic hysteresis loops at 10 K and 20 K, for magnetic fields up to 7 T. Owing to the AFM ground state, negligible hysteresis effect is found for the magnetic hysteresis loop at 10 K and 20 K, which will not produce heat loss and is very favorable for the actual application of magnetic refrigerant. AFM ordering in this compound below T_N is ensured by the crossover among the curves observed in Figures 3 and 4.

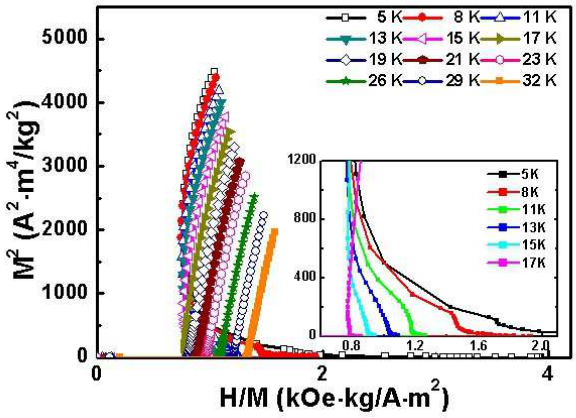

Figure 5. *Arrott-plots of $TbFe_2Al_{10}$ measured during field increasing. The inset displays the enlarged part of Arrott-plots below T_N.*

Figure 5 presents the Arrott-plots (M^2 VS H/M) for $TbFe_2Al_{10}$ compound derived from the data in Figure 3. The inset presents enlarged part of Arrott-plots below T_N. The negative slope in the low temperature region showed in the inset of Figure 5 further confirms the occurrence of a first ordering phase transition according to the Banerjee criterion. [21] This corresponds to the antiferromagnetic ground state and the magnetic transformation in this material.

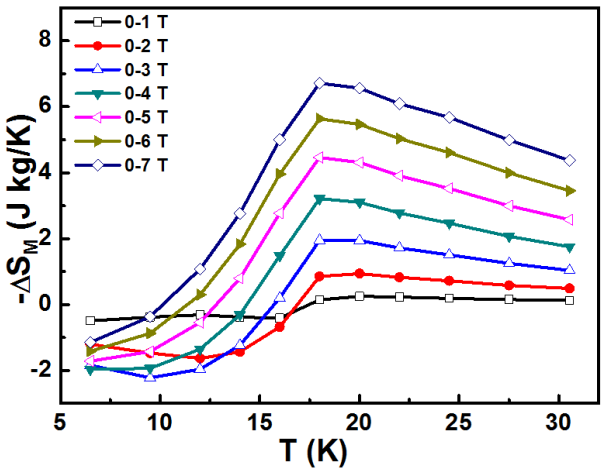

Figure 6. *Magnetic entropy changes as a function of temperature for $TbFe_2Al_{10}$ compound under various magnetic field changes (ΔS-T).*

The isothermal magnetic entropy changes have been calculated from the isothermal magnetization data by employing Maxwell's relationship:

$$\Delta S = \int_0^H (\partial M/\partial T)_H \, dH \quad (1)$$

The ΔS for different magnetic field changes as a function of temperature (ΔS-T) of $TbFe_2Al_{10}$ is shown in Figure 6. Similar to other magnetocaloric materials, the peak value of magnetic entropy occurs near the phase transition temperature at 18 K, and the maximum magnetic entropy changes (ΔS) of 0-5 T and 0-7 T magnetic field changes are -4.5 J/kg K and –6.7 J/kg K, respectively. It is worth noting that under low temperature and low magnetic field changes, positive values were found in the magnetic entropy changes (ΔS), which also corresponds to the antiferromagnetic ground state of the material. What catches our attentions is that the peak values of ΔS for $TbFe_2Al_{10}$ can compete with the other popularly researched magnetic refrigerant materials such as $GdPd_2Si$ (–8.6 J/kg K) and RNi_5 (~8 J/kg K) in low temperature regime under the same field changes [22, 23].

4. Conclusion

In summary, we prepared $TbFe_2Al_{10}$ sample with pure orthogonal $SmFe_2Al_{10}$ structure by arc melting and long-time annealing, and the magnetic properties and magnetocaloric effects were studied. The results show that the ground state of the sample is antiferromagnetic with Néel temperature T_N=18 K. At the 5K temperature, two variable magnetic transitions of antiferromagnetic-ferrimagnetic and ferrimagnetic-ferromagnetic occurred at 0.95 T and 1.89 T, respectively. The maximum magnetic entropy change (ΔS) of 0-5 T and 0-7 T magnetic field are -4.5 J/kg K and -6.7 J/kg K, respectively. In conclusion, low rare earth content, good toughness, no hysteresis and large magnetocaloric effect make $TbFe_2Al_{10}$ sample a promising magnetic refrigerant.

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