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Complicated magnetic phase transitions and Large magnetocaloric effects (MCEs) in RCoGe (R=Tb, Dy) compounds have been reported in this paper. Results show that the TbCoGe compounds have a magnetic phase transition from antiferromagnetic to paramagnetic (AFM-PM) at $T_N \sim 16$ K, which is close to the value reported by neutron diffraction. The DyCoGe compound undergoes complicated phase changes from 2 K up to 300 K. The peak at 10 K displays a phase transition from antiferromagnetic to ferromagnetic (AFM-FM). In particular, a significant ferromagnetic to paramagnetic (FM-PM) phase transition was found at the temperature as high as 175 K and the cusp becomes more abrupt with the magnetic field increasing from 0.01 T to 0.1 T. The maximum value of magnetic entropy change of TbCoGe and DyCoGe compounds achieve 14.5 J/kg K and 11.5 J/kg K respectively for a field change of 0-5 T. Additionally, the correspondingly considerable refrigerant capacity value of 260 J/kg and 242 J/kg are also obtained respectively, suggesting that both TbCoGe and DyCoGe compounds could be considered as good candidates for low temperature magnetic refrigerant. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5007114

I. INTRODUCTION

Since Thomson firstly predicted magnetocaloric effect (MCE) in 1860,¹ and decades later Weiss and Piccard discovered it experimentally,² magnetic refrigeration based on magnetocaloric effect (MCE) has attracted tremendous attention due to its energy-efficient and environment-friendly advantages as compared with the common gas-compression refrigeration technology. Magnetic refrigeration has achieved great success in ultra-low temperature.^{3,4} Recently, it has been anticipated to be widely used in room temperature in the near future.⁵ Many excellent magnetocaloric materials have been reported in detailed, such as $Gd_5Si_2Ge_2$, $MnFeP_{1-x}As_x$, $MnAs_{1-x}Sb_x$, $La(Fe, M)_{13}(M=Si, Al)$, and NiMnGa.^{6–11} In addition to common applications such as domestic refrigerators, many materials showing large ΔS_M in low temperature range have also been studied, as they are important for basic research as well as special technological applications.^{12–16}

The RTX (R = rare earth, T = transition metal, and X = p-block metal) family compounds with various crystalline structures have been explored extensively because of their rich magnetic and electrical transport properties.^{17–19} Recently, lots of attentions have been paid to



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their large magnetocaloric effect(MCE) especially at low temperatures.^{20–28} Investigations by power X-ray diffraction, susceptibility measurements and neutron diffraction experiments on the ternary RCoSi (R=La-Sm, Ga, Tb) and RCoGe (R=La-Nd) compounds are reported.^{29,30} Results show they crystalline in the well-known tetragonal CeFeSi-type structure (space group P4/nmm) which is closely related to the ThCr₂Si₂ structure and can be described as isolated "ThCr₂Si₂ blocks" (BaAl₄ slab) connected via R-R contacts (CrB slab). Whereas RCoSi (R=Ho, Er, Dy) and RCoGe (R=Sm, Gd-Er) compounds are orthorhombic TiNiSi-type structure (space group Pnma 62).^{25,31–37} So they display different magnetic properties. In this paper, we will report the large MCEs and the complicated magnetic phase transitions in RCoGe (R=Tb, Dy) compounds.

II. EXPERIMENTAL DETAILS

Polycrystalline DyCoGe and TbCoGe compounds were synthesized by arc-melting the stoichiometric mixture of constituent elements Dy/Tb, Co, and Ge with high-purity under purified argon atmosphere. 3 at% excessive rare earths were added to compensate the weight loss during the arcmelting. These ingots were re-melted several times to ensure their homogeneity. Then these samples were annealed in a quartz tube filled with high-purity argon atmosphere for two weeks at 900 K to improve the homogeneity. Phase purity and crystal structure of annealed samples were checked by Powder X-ray diffraction (XRD) using Cu Ka radiation at room temperature. Magnetizations were carried out on a commercial MPMS SQUID VSM magnetometer and a commercial MPMS-XL SQUID magnetometer (Quantum Design).

III. RESULTS AND DISCUSSION

The powder XRD patterns of TbCoGe and DyCoGe compounds at room temperature are shown in Fig. 1. The results indicate both polycrystalline TbCoGe and DyCoGe compounds are of single phase with an orthorhombic TiNiSi-type structure (space group Pnma 62, Z=4). The lattice parameters are almost in agreement with the previous report.



FIG. 1. The powder XRD patterns of TbCoGe and DyCoGe compounds at room temperature.



FIG. 2. a Temperature dependences of magnetizations of TbCoGe under 0.01 T. The inset displays the inverse susceptibility transformed from the MT curve of TbCoGe and the solid line to inverse susceptibility shows the CW fit under 0.01 T. Fig. 2b shows MT curves of DyCoGe compounds under 0.01 T, 0.05 T and 0.1 T, respectively. Fig. 2c shows Powder XRD patterns of DyCoGe compounds at different temperatures.

The temperature dependence of magnetization was measured in zero-field-cooling (ZFC) mode for TbCoGe compounds under the field of 0.01T, as shown in figure 2a. The Neel temperature (T_N) determined by the peak position of M-T curve is 16 K, close to the value reported by neutron diffraction in Ref. 29. Whereas the obvious change at 12 K marked as T_t on the M-T curve has not been explained. Neutron diffraction studies revealed the coexistence of noncollinear FM and a sine-modulated antiferromagnetic (AFM) ordering for TbCoGe, the competition of FM and AFM interactions may lead to this abrupt at T_t. The inverse susceptibility $1/\chi$ as a function of temperature under 0.01 T is plotted in the inset of figure 2a. It is clear that the inverse magnetic susceptibility of TbCoGe deviates from the Curie–Weiss (CW) law around 160 K, which implies the formation of finite-sized FM clusters in the matrix of the PM phase.

Figure 2b shows the temperature dependence of magnetization for the DyCoGe compound under the fields of 0.01 T, 0.05 T and 0.1 T, respectively. Several cusps indicate DyCoGe undergoes complicated phase changes from 2 K up to 300 K. From M–T curves at 0.01 T, we can speculate that the sharp change at 10 K is corresponding to a magnetic phase from antiferromagnetic to ferromagnetic (AFM-FM). The transition at lower temperature is considered to be caused by many competing forces. In particular, a significant ferromagnetic to paramagnetic (FM-PM) phase transition was found at the temperature as high as 175 K, which is similar to that of HoCoGe and RCoSi (R=Gd, Tb) compounds.^{29,32} The difference is the cusp of DyCoGe becomes more abrupt with the magnetic field increasing from 0.01 T to 0.1 T. We also suspect a structural phase transition occurs with temperature increasing, but we have found no any peak appearing or vanishing from the powder XRD patterns of DyCoGe around all of the phase transition temperatures, as shown in Fig. 2c. Table I shows the magnetic phase transition temperatures and crystal structures of RCoX (R=La-Sm, Gd-Er; X=Si, Ge) compounds.^{29–37} We will continue to have a deep research about the interesting magnetic phase changes in RCoGe (R=Gd~Er) compounds in the future.

The magnetization isotherms taken at different temperatures from 0 T to 5 T field are shown in Fig. 3a. The magnetization is not saturated at 5 T field, but it shows a tendency to get saturated at higher field. The significant change in the slope of magnetization isotherms near T_N is expected to result in significant magnetic entropy change. To make it clear, partially enlarged view is shown up in the inset of Fig. 3a. Below the temperatures T_N , the magnetization curve shows a linear increase and then a sudden jump with increasing magnetic field, indicating the metamagnetic transition from AFM to FM phase. The negative slope of the Arrott plot confirmed the occurrence of a first-order

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Compound	$Tc \pm l(K)$	Crystal Structure	ΔS_M (J/kg K)	RC (J/kg)			Crustal	ΔS_M (J/kg K)	RC (J/kg)
			0-5T		Compound	$Tc \pm l(K)$	Structure	0-5T	
LaCoSi ²⁹	-	Tetragonal -CeFeSi	-	-	LaCoGe ³⁰	-	Tetragonal -CeFeSi	-	-
CeCoSi ²⁹	-		-	-	CeCoGe ³⁰	_		-	-
PrCoSi ²⁹	-		-	-	PrCoGe ³⁰	-		-	-
NdCoSi ²⁹	$T_N = 7$		-	-	NdCoGe ³⁰	$T_N = 8$		-	-
SmCoSi ²⁹	$T_N = 15$		-	-	SmCoGe ³⁵	-	Ortho -TiNiSi	-	-
GdCoSi ²⁹	$T_N = 175$		-	-	GdCoGe ³⁶	_		-	-
TbCoSi ²⁹	$T_N = 140$		-	-	TbCoGe ^{this}	$T_N = 17$		14.5	260
DyCoSi ^{33,34}	$T_N = 159$	Ortho -TiNiSi	-	-	DyCoGe ^{this}	$T_t = 10$ $T_c = 175$		11.5	242
HoCoSi ^{31,34}	<i>Tc</i> =15		28.2	474	HoCoGe ³²	Tc=7.6 $T_t=170$		23.9	402
ErCoSi ³⁴	<i>Tc</i> =5.5		25	372	ErCoGe ³⁷	-		-	-

TABLE I. Curie temperature, crystal structure and MCEs of RCoX (R=La-Sm, Gd-Er; X=Si, Ge) compounds.

phase transition.³⁸ Generally speaking, metamagnetic transition from AFM ground state to FM state belonged to first-order transition. The critical field of metamagnetic transition about the magnetization curve at 2 K was 1.3 T, determined by the maximum value of $\partial M/\partial H$. With temperature increasing to T_N, the AFM state change to FM state completely. Magnetic entropy changes of TbCoGe compound in different magnetic fields were calculated using the Maxwell relation $\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH$ based on the magnetization isotherms. Positive values of ΔS_M were found in low temperatures, as figure 3b displayed, corresponding to the AFM nature of TbCoGe. The maximum values of ΔSM reach 7.5 J/kg K and 14.5 J/kg K for the field changes of 0-2 T and 0-5 T, respectively. Refrigerant capacity (RC) is considered as another important parameter that characterizes the refrigerant efficiency. It was estimated by using the approach $RC = \int_{T_{\text{tot}}}^{T_{\text{hot}}} |\Delta S_M| dT$, where T_{cold} and T_{hot} are the temperatures corresponding to the both sides of half maximum value of ΔS_M peak. RC values are 80 J/kg and 260 J/kg for the field changes of 0-2 T and 0-5 T, respectively.

Similarly, the magnetocaloric properties of DyCoGe samplers have been analyzed. The magnetization isotherms under typical fields are shown in figure 4a. According to the Banerjee criterion, the plot of M^2 vs. H/M shows negative slope suggesting first-order magnetic phase transition. The crossovers among the curves also verified the AFM ordering in this compound. The values of ΔS_M peak reach 6 J/kg K and 11.5 J/kg K for the field change of 0-2 T and 0-5 T, respectively, as shown in figure 4b.



FIG. 3. a shows Magnetic isothermals measured during field increasing for TbCoGe compound around T_N . The inset shows the enlarged magnetic isothermals below T_N . Fig. 3b shows magnetic entropy changes of TbCoGe compound calculated from magnetization under typical magnetic field changes.



FIG. 4. a shows magnetic isothermals of DyCoGe compound in a temperature range of $5 \sim 50$ K measured during field increasing. Fig. 4b shows magnetic entropy change of DyCoGe compound under magnetic field changes of 0–2, 0–3, 0–4, and 0–5 T, respectively.

It was evident that both the peak values of ΔS_M of TbCoGe and DyCoGe compounds were competitive to the other potential magnetic refrigerant materials in low temperature range.

IV. CONCLUSION

In conclusion, both the TbCoGe and DyCoGe compounds crystallizes in TiNiSi-type orthorhombic structure. A competitive MCE and large RC in RCoGe (R=Tb, Dy) compounds were observed. For a field change of 0–5 T, the maximum values of ΔS_M are 14.5 J/kg K and 11.5 J/kg K, and RC values are 260 J/kg and 242 J/kg, for TbCoGe and DyCoGe compounds respectively. The excellent performances indicate the RCoGe (R=Tb, Dy) compounds are attractive candidates for magnetic refrigeration in the low temperature range.

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- ¹ W. Thomson, Cyclopedia of the Physical Sciences (1860), p. 838.
- ² P. Weiss and A. Piccard, J. Phys. 7, 103 (1917).
- ³ W. F. Giauque and D. P. MacDougall, Phys. Rev. **43**, 0768 (1933).
- ⁴ A. H. Cooke, H. J. Duffus, and W. P. Wolf, Philos. Mag. 44, 623 (1953).
- ⁵ K. A. Gschneidner, Jr., V. K. Pecharsky, and A. O. Tsokol, Rep. Prog. Phys. 2005, 68 (1479).
- ⁶ V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).
- ⁷ H. Wada and Y. Tanabe, Appl. Phys. Lett. **79**, 3302 (2001).
- ⁸ O. Tegus, E. Brück, K. H. J. Buschow, and F. R. de Boer, Nature **415**, 150 (2002).
- ⁹ F. X. Hu, B. G. Shen, J. R. Sun, Z. H. Chen, G. H. Rao, and X. X. Zhang, Appl. Phys. Lett. 78, 3675 (2001).
- ¹⁰ B. G. Shen, F. X. Hu, Q. Y. Dong, and J. R. Sun, Chin. Phys. B 22, 017502 (2013).
- ¹¹ F. X. Hu, B. G. Shen, and J. R. Sun, Appl. Phys. Lett. **76**, 3460 (2000).
- ¹² K. A. Gschneidner, Jr., V. K. Pecharsky, and A. O. Tsokol, Rep. Prog. Phys. 68, 1479 (2005).
- ¹³ X. Q. Zheng, X. P. Shao, J. Chen, Z. Y. Xu, F. X. Hu, J. R. Sun, and B. G. Shen, Appl. Phys. Lett. **102**, 022421 (2013).
- ¹⁴ X. Q. Zheng, J. Shen, F. X. Hu, J. R. Sun, and B. G. Shen, Acta Phys. Sin. **65**, 217502 (2016).
- ¹⁵ X. Q. Zheng and B. G. Shen, Chin. Phys. B **26**, 027501 (2017).
- ¹⁶ J. Chen, B. G. Shen, Q. Y. Dong, F. X. Hu, and J. R. Sun, Appl. Phys. Lett. **95**, 132504 (2009).
- ¹⁷ A. Szytula, in *Handbook of Magnetic Materials*, ed. K. H. J. Bushcow, Elsevier, New York, **6**, 85 (1991).
- ¹⁸ S. Gupta and K. G. Suresh, J. Alloys Compd. **618**, 562 (2015).
- ¹⁹ H. Zhang and B. G. Shen, Chin. Phys. B 24, 127504 (2015).
- ²⁰ X. X. Zhang, F. W. Wang, and G. H. Wen, J. Phys. Condens. Matter. **13**, L747 (2001).
- ²¹ N. K. Singh, K. G. Suresh, R. Nirmala, A. K. Nigam, and S. K. Malik, J. Appl. Phys. 101, 093904 (2007).
- ²² J. Chen, B. G. Shen, Q. Y. Dong, F. X. Hu, and J. R. Sun, Appl. Phys. Lett. **96**, 152501 (2010).
- ²³ Q. Y. Dong, J. Chen, J. Shen, J. R. Sun, and B. G. Shen, J. Magn. Magn. Mater. **324**, 2676 (2012).
- ²⁴ S. B. Gupta and K. G. Suresh, Appl. Phys. Lett. **102**, 022408 (2013).

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²⁵ S. Gupta and K. G. Suresh, Mater. Lett. 113, 195 (2013).

- ²⁶ S. B. Gupta, R. Rawat, and K. G. Suresh, Appl. Phys. Lett. **105**, 012403 (2014).
 ²⁷ 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).
- ²⁸ H. Zhang, Y. W. Li, E. K. Liu, Y. J. Ke, J. L. Jin, Y. Long, and B. G. Shen, Sci. Rep. 5, 11929 (2015).
- ²⁹ R. Welter, G. Venturini, E. Ressouche, and B. Malaman, J. Alloys Compd. 210, 279 (1994).
- ³⁰ R. Welter, G. Venturini, and B. Malaman, J. Alloys Compd. 201, 191 (1993).
- ³¹ J. Leciejewicz, N. Stüsser, M. Kolenda, A. Szytula, and A. Zygmunt, J. Alloys Compd. 240, 164 (1996).
- ³² Y. Zhang, Q. Y. Dong, L. C. Wang, M. Zhang, H. T. Yan, J. R. Sun, F. X. Hu, and B. G. Shen, RSC Adv. 6, 106171 (2016). ³³ I. Ijjaali, R. Welter, G. Venturini, and B. Malaman, J. Alloys Compd. 292, 4 (1999).
- ³⁴ Z. Y. Xu, "Magnetism and magnetocaloric effects in rare earth transition metal compounds with low temperature transition," Ph. D. thesis, Graduate University of Chinese Academy of Sciences, 2012.
- ³⁵O. Y. Mruz, V. K. Belskii, Y. K. Gorelenko, R. V. Skolozdra, and O. I. Bochek, Ukrainskii Fizicheskii Zhurnal (Russian Edition) 32, 1856 (1987).
- ³⁶ Y. K. Gorelenko, P. K. Starodub, V. A. Bruskov, R. V. Skolozdra, V. I. Yarovets, O. I. Bodak, and V. K. Pecharskii, Ukrainskii Fizicheskii Zhurnal (Russian Edition) 29, 867 (1984).
- ³⁷ A. E. Dwight, P. P. Vaishnava, C. W. Kimball, and J. L. Matykiewicz, Journal of the Less-Common Metals **119**, 319 (1986). ³⁸ S. K. Banerjee, Phys. Lett. 12, 16 (1964).