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Cite as: J. Appl. Phys. **125**, 225102 (2019); https://doi.org/10.1063/1.5090388 Submitted: 27 January 2019 . Accepted: 21 May 2019 . Published Online: 10 June 2019

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Low working temperature near liquid helium boiling point of $RNiAl_2$ (R = Tm, Tb and Gd) compounds with large magnetocaloric effect

Cite as: J. Appl. Phys. **125**, 225102 (2019); doi: 10.1063/1.5090388 Submitted: 27 January 2019 · Accepted: 21 May 2019 · Published Online: 10 June 2019



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ABSTRACT

A polycrystalline TmNiAl₂ compound with transition temperature near the liquid helium boiling point was successfully synthesized. Magnetic measurements show that FM (ferromagnetic) to FM and FM to PM (paramagnetic) transitions take place at 2.4 K and 4.0 K, respectively. Magnetic entropy change $(-\Delta S_M)$ is calculated, and its maximal value $[(-\Delta S_M)_{max}]$ reaches as high as 20.7 J/kg K with the field change of 0–5 T. The low transition temperature together with large $(-\Delta S_M)_{max}$ at the liquid helium temperature zone originates from the weak spin-spin exchange interaction between Tm atoms. For a clear comparison, the magnetocaloric effect (MCE) of polycrystalline RNiAl₂ (R = Tb and Gd) samples was also prepared and investigated. For the TbNiAl₂ compound, FIM (ferrimagnetic) to AFM (antiferromagnetic) and AFM to PM transitions occur at 11.0 K and 21.5 K, respectively. As for the GdNiAl₂ compound, an FM to PM transition occurs at 30.5 K. The value of $(-\Delta S_M)_{max}$ under the field change of 0–5 T is calculated to be 11.8 J/kg K and 17.3 J/kg K for TbNiAl₂ and GdNiAl₂, respectively. Compared with other RNiAl₂-series MCE materials, TmNiAl₂ exhibits the lowest working temperature and relatively larger $(-\Delta S_M)_{max}$. The large MCE at low temperature indicates that TmNiAl₂ is competitive among the MCE materials working at a liquid helium temperature zone.

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I. INTRODUCTION

Traditional refrigeration technology is based on gas expansion/compression, leading to some issues which cannot be ignored, such as environmental issues and energy efficiency. Magnetic refrigeration technology based on the magnetocaloric effect (MCE) provides an alternative for refrigeration applications with advantages, such as environmental friendliness and high energy efficiency. One of the main contents in the field of magnetic refrigeration research is to explore and/or synthesize magnetic materials with large MCE. Up to now, many kinds of magnetic materials including LaFeSi, GdSiGe, MnAs, MnFePAs, and NiMnSn based on first-order magnetic transitions^{1–7} were studied for the large MCE at room temperature. Recently, low-temperature magnetic refrigerant materials have also attracted extensive attention because of the underlying applications in liquefaction of gas and low temperature construction. Representatively, low-temperature MCE materials mainly include ErGa, Ho₂Cu₂Cd, Dy₂Cu₂In, Gd₂CuSi₃, Ho₅Pd₂, Tb₃Co, ErAl₂, ErCo₂, ErAgAl, HoCuGe, HoCuSi, TmZn, and ErRuSi.^{8–20} For applications, some challenges should be overcome, such as higher thermal reversibility and larger MCE. In particular, it is of great importance to synthesize and study MCE materials working at a low-temperature zone near the boiling point of liquid helium. One of the choices is to explore these MCE materials among the rare earth based compounds.

For the past few decades, the ternary intermetallic RNiAl₂ (R-rare earth) compounds were extensively investigated with a focus on their magnetic properties. RNiAl₂ (R-rare earth) compounds exhibit an orthorhombic MgCuAl2-type structure with the space group Cmcm.²¹ Low transition temperatures and complex magnetic transitions were observed in this series of materials.² For example, the magnetic properties and critical behavior of the GdNiAl₂ compound were studied.²⁵ The MCE curve with a platform was observed in the GdNiAl₂ compound with few Gd₁Ni₂Al₃ phases, and it was claimed that there was only one FM (ferromagnetic) to PM (paramagnetic) transition around 28 K.²⁴ The magnetic properties of the TbNiAl₂ compound were investigated by magnetic measurements and neutron diffraction techniques. Two successive transitions were observed at 11.7 K and 20 K.²³ More recently, the magnetic properties and magnetocaloric effect of HoNiAl₂ and ErNiAl₂ have been reported.²

As important members of the RNiAl₂ family, it is necessary to synthesize and investigate RNiAl₂ (R = Tm, Tb, Gd) compounds in detail. The TmNiAl₂ compound has not been reported, to the best of our knowledge, which is expected to show a low transition temperature. The MCE of the TbNiAl₂ compound based on successive magnetic transitions has not been studied although its magnetic properties were reported. Further analysis of magnetic transitions and the MCE peak of the GdNiAl₂ compound should be carried out even if its MCE was reported. Here, a detailed study on the family of RNiAl₂ (R = Tm, Tb, and Gd) compounds will be presented. For the TmNiAl₂ sample, the maximal magnetic entropy change [($-\Delta S_M$)_{max}] reaches as high as 20.7 J/kg K at low temperatures in the field change of 0–5 T.

II. EXPERIMENTAL DETAILS

The RNiAl₂ (R = Tm, Tb, and Gd) ingots were prepared in a high-purity argon atmosphere by arc-melting the stoichiometric amounts of high-purity (>99.9 wt. %) starting metals on a water cooled copper hearth. To achieve compositional homogeneity, the obtained ingot was wrapped in a molybdenum foil, sealed in a high-vacuum quartz tube, annealed at 800 °C for 7 days, and then quenched into liquid nitrogen. The phase purity, crystal structure, and lattice parameters were examined by the Rietveld refinement of powder x-ray diffraction (XRD) data collected at room temperature using the Cu $K\alpha$ radiation. The chemical composition of the samples was examined by a scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS). Magnetic measurements were carried out as functions of temperature and magnetic field by using a vibrating sample magnetometer based on quantum design (SQUID-VSM).

III. RESULTS AND DISCUSSION

The XRD patterns of $RNiAl_2$ (R = Tm, Tb, and Gd) compounds were obtained at room temperature and then were fitted by the Rietveld refinement method, which are shown in Fig. 1. Reduced chi-square, wRp, and Rp were also obtained and shown in Fig. 1. Refinement results indicate that all the samples have an orthorhombic MgCuAl₂-type structure with the space group Cmcm, and no other Bragg reflections corresponding to impurity phases were observed. It is worth pointing out that no Gd₁Ni₂Al₃ phase was observed in the GdNiAl₂ compound, indicating that a more pure GdNiAl₂ compound is obtained compared with a previous work.²⁴ The chemical composition of RNiAl₂ (R = Tm, Tb, and Gd) compounds was examined by SEM with EDS. The results show that the atom ratio of R, Ni, and Al is (25.1:26.3:48.6), (21.8:24.4:53.7), and (23.8:26.6:49.7) for TmNiAl₂, TbNiAl₂, and GdNiAl₂ compounds, respectively, close to the nominal chemical composition. Detailed results show that both R atoms and Ni atoms occupy the same crystallographic 4c sites with the m2m point symmetry described as (0, 0, 0; 0.5, 0.5, 0) + (0, y, 0.25; 0, -y, 0.75), and Al atoms occupy the crystallographic 8f sites with the m.. site symmetry described as (0, 0, 0; 0.5, 0.5, 0) + (0, y, z; 0, -y, z + 0.5; 0, y, -z + 0.5; 0, -y, -z).The crystal structure of RNiAl₂ compounds is shown in Fig. 2. In addition, the atom ratios of TmNiAl2, TbNiAl2, and GdNiAl2 compounds are only nominal values. It is well known that rare earth elements are volatile during the process of smelting. Therefore, vacancies are very common in rare earth based compounds. According to the XRD refinement, the vacancies of rare earth atoms are calculated to be 1.02%, 0.74%, and 0.89% in TmNiAl₂, TbNiAl₂,



FIG. 1. Powder X-ray diffraction patterns for (a) $\mathsf{TmNiAl}_2,$ (b) $\mathsf{TbNiAl}_2,$ and (c) $\mathsf{GdNiAl}_2.$



FIG. 2. Crystal structure of RNiAl₂ compounds.

and GdNiAl₂ compounds, respectively. The lattice parameters are listed in Table I. The lattice parameters including a, b, and c all show a monotonous decrease with increasing atomic number R.

Temperature dependences of the magnetization at zero field cooled (ZFC) and field cooled (FC) under a magnetic field of 0.01 T for $RNiAl_2$ (R = Tm, Tb, Gd) compounds are shown in Fig. 3. For the M-T curve of the TmNiAl₂ compound [Fig. 3(a)], a plateau takes place near 4 K as the temperature decreases, indicating the first magnetic phase transition. With the temperature decreasing further, magnetization increases rapidly, indicating the second magnetic transition. The temperature of magnetic transitions was determined to be 2.4 K and 4.0 K, according to the maximum value of the first derivative of M-T curves. Accordingly, the magnetic transitions are FM to FM transition and FM to PM transition, respectively, based on the discussion below. It is worth noting that both order-order transition temperature and order-disorder transition temperature are very low, and they are in the temperature range around the liquid helium boiling point. For the TbNiAl₂ compound shown in Fig. 3(b), two successive magnetic transitions can be observed clearly on M-T curves. Two magnetic transitions are FM to AFM transition and AFM to PM transition according to the literature.²³ The FM to AFM transition temperature (T_t) was determined to be 11.0 K according to the maximum value of the first derivative of M-T curves, and the AFM to PM transition temperature also known as the Néel temperature (T_N) was determined to be 21.5 K according to the maximum value of magnetization in the higher temperature region. The above two transition temperatures are in good agreement with the previous results.²¹

TABLE I. The lattice parameters of RNiAl₂ compounds (R = Tm, Tb, and Gd).

Samples	a (Å)	b (Å)	c (Å)	References
TmNiAl ₂	4.0472(1)	9.9687(3)	6.8286(2)	This work
GdNiAl ₂	4.0595(2) 4.0632(2)	10.2610(4) 10.3760(5)	6.8657(3) 6.8820(4)	This work This work
TbNiAl ₂ GdNiAl ₂	4.042(1) 4.0725(6)	10.263(1) 10.3983(2)	6.893(2) 6.8942(2)	23 24
Gartiniz	1.0725(0)	10.5905(2)	0.09 12(2)	





FIG. 3. Temperature dependences of zero field cooled (ZFC) and field cooled (FC) magnetization under the field of 0.01 T for (a) TmNiAl₂, (b) TbNiAl₂, and (c) GdNiAl₂ compounds. Insets are the linear fitting of the relationship between temperature and reciprocal susceptibility.

The magnetic structures are commensurate ferrimagnetic (FIM) below T_t and incommensurate AFM between T_t and T_N according to the neutron diffraction experiment.²³ In order to further confirm the phase transition of TbNiAl₂, AC susceptibility was also measured and shown in Fig. 4(a). It can be seen that there are two peaks at 10.0 and 23.0 K both in the real component (χ') and in the imaginary component (χ'') of the AC susceptibility, corresponding to the two magnetic transitions, respectively. The values of magnetic transitions obtained from AC susceptibility are close to the results obtained from DC measurements. The temperature dependence of reciprocal susceptibility of the TbNiAl₂ compound is shown in the inset of Fig. 3(b). The effective magnetic moment of the Tb atom is calculated to be $9.2\,\mu_{\rm B}$, close to the theoretical value of 9.7 $\mu_{\rm B}$. For M-T curves of GdNiAl₂ shown in Fig. 3(c), one sharp decrease was clearly observed with the increasing temperature, indicating a magnetic transition. In order to further study the

magnetic phase transition of the GdNiAl₂ compound, AC susceptibility at the frequency of 47 Hz with an oscillation field of 5 Oe was measured and shown in Fig. 4(b). Only one peak was observed around 26.5 K on the imaginary (χ'') component of the AC curve and also only one peak was observed around 29.0 K on the real component (χ') of the AC curve. The peak of the AC curve comes from FM-PM transition, and the Curie temperature is calculated to be 30.5 K according to the maximum value of the first derivative of the M-T curve. The transition temperature was close to that reported in previous works.^{22,24} The linear relationship between the temperature and the reciprocal susceptibility in the temperature region above T_C indicates that the Curie-Weiss law is valid in PM state. The effective magnetic moment (μ_{eff}) of Gd is calculated to be 7.6 $\mu_{\rm B}$ according to the linear fitting, in good agreement with the theoretical value of 7.8 $\mu_{\rm B}$. In addition, it should be noted that good thermal reversibility is observed around T_C or T_N for three RNiAl₂ (R = Tm, Tb, Gd) compounds.

The above results also show that the order to disorder transition temperatures has a monotonous decrease with the increasing rare earth atomic number. Generally, the order to disorder transition temperature depends on the strength of magnetic exchange interaction and, thus, it is related to both the spin of magnetic atoms and their distance. For rare earth based compounds, the spin of rare earth atoms always plays a dominant role in the order to disorder transition temperatures. To be specific, there is a positive correlation between the spin of a rare earth atom and the magnetic exchange interaction. It is known that the magnetic exchange interaction plays a direct influence on the order to disorder transition temperature. Therefore, the larger the spin of rare earth atom is, the higher the order to disorder transition temperature is, such as $Gd_xEr_{1-x}Ga$ and $Ho_xEr_{1-x}Ni$ series.^{27,28} For RNiAl₂ (R = Tm, Tb, Gd) compounds, the Gd atom has the largest spin, which shows the largest order to disorder transition temperature for the GdNiAl₂ compound. The Tm atom has the smallest spin, leading to the smallest order to disorder transition temperature for the TmNiAl₂ compound.

The magnetization isotherms of $RNiAl_2$ (R = Tm, Tb, Gd) compounds were measured under magnetic fields up to 5 T at various temperatures as shown in Fig. 5. The isothermal magnetization curves of the TmNiAl₂ compound are shown in Fig. 5(a), and the M-H curves at low temperatures in a lower field range are



FIG. 4. Temperature dependences of the real component (χ') and the imaginary component (χ'') of the AC magnetic susceptibility at the frequency of 9 Hz with an oscillation field of 10 Oe for (a) the TbNiAl₂ compound and at the frequency of 47 Hz with an oscillation field of 5 Oe for (b) GdNiAl₂.



FIG. 5. Isothermal magnetization curves at different temperatures with applied fields up to 5 T for (a) TmNiAl₂, (b) TbNiAl₂, and (c) GdNiAl₂. Insets are the enlarged view of some selected M-H curves.

presented in the inset of Fig. 5(a). A characteristic of the FM state was observed for all M-H curves below T_C. Therefore, the magnetic transition at 2.4 K is FM to FM transition. However, a more complex M-H curve was observed at 2.2 K. The magnetization curve exhibits a rapid increase first and then slows down, resulting in a platform. With further increasing magnetic fields, the magnetization increases rapidly again, and finally it reaches a saturation value of $6.0 \mu_{\rm B}$. The two-stage magnetizing process may result from out of sync ordering of Tm and Ni atomic moments. The isothermal magnetization curves of the TbNiAl₂ compound are shown in Fig. 5(b), and the M-H curves at low temperatures in a lower field range are presented in the inset of Fig. 5(b). The positive correlation between magnetization and temperature in the low field range indicates the existence of the AFM order in the temperature range below 10 K, which is similar to the M-H curves of the Er₁₂Co₇ compound.²⁹ However, typical FM characteristic rather than AFM characteristic is observed for every single magnetization curve at low temperatures, such as the M-H curve at 10 K. The above result is in accordance with that obtained from neutron diffraction experiments, indicating that commensurate FIM ground state exists at low temperatures.²⁵ In the temperature range between 10 K and 20 K, M-H curves show typical AFM characteristic. In the first stage, magnetization increases slowly at low fields. In the second stage, the magnetization increases quickly when the magnetic field exceeds a critical value. In the third stage, the magnetization tends to be saturated further increasing the fields. That is, the magnetic



FIG. 6. Temperature dependences of magnetic entropy change $(-\Delta S_M)$ for RNiAl₂ (R = Gd, Tb, and Tm) compounds under field changes of (a) 0–2 T and (b) 0–5 T.

ground state is AFM and a metamagnetic transition behavior can be observed at the temperature range between 10 K and 20 K. The incommensurate AFM structure in this temperature zone has been confirmed by the neutron diffraction technique.²⁵ Therefore, the TbNiAl₂ compound undergoes an FIM to AFM transition and an AFM to PM transition with increasing temperature. For M-H curves of the GdNiAl₂ compound below T_C, the magnetization shows a rapid increase at low fields and tends to saturate with further increasing fields, indicating a typical FM characteristic below T_C [Fig. 5(c)]. Therefore, the magnetic ground state in the whole temperature range below T_C is FM for the GdNiAl₂ compound. As a result, the magnetic transition at 30.5 K is the FM-PM transition.

Temperature dependences of the magnetic entropy change $(-\Delta S_M)$ for RNiAl₂ (R = Tm, Tb, Gd) compounds were calculated from M-H data by the Maxwell relation: $\Delta S_M(T, H) = -\int_{H_1}^{H_2} \frac{\partial M}{\partial T} dH$, where H₁ and H₂ are the initial and the final magnetic fields, respectively. The $-\Delta S_M$ curves under field changes of 0–2 T and 0–5 T for



FIG. 7. Arrott plots of (a) TmNiAl₂, (b) TbNiAl₂, and (c) GdNiAl₂ compounds.

RNiAl₂ compounds are shown in Fig. 6. The maximal value of magnetic entropy change $[(-\Delta S_M)_{max}]$ under a magnetic field change of 0-2 T is calculated to be 14.5, 6.8, and 9.4 J/kg K for TmNiAl₂, TbNiAl₂, and GdNiAl₂, respectively. As for 0-5 T field change, $(-\Delta S_M)_{max}$ is calculated to be 20.7, 11.8, and 17.3 J/kg K accordingly. The TmNiAl₂ compound shows a much larger $(-\Delta S_M)_{max}$ than GdNiAl₂ and TbNiAl₂ compounds. According to the theory presented by Oesterreicher and Parker, the compound with a smaller order to disorder transition temperature usually shows a larger $-\Delta S_M$ if the differences of the saturation magnetizations are not large compared with other samples.³⁰ This deduction is not very strict, but it can simply interpret some result of rare earth based MCE materials such as Gd_xEr_{1-x}Ga and Ho_xEr_{1-x}Ni series.^{27,28} The TmNiAl₂ compound has the smallest order to disorder transition temperature among the RNiAl₂ (R = Tm, Tb, Gd) compounds, and their saturation magnetization has a little variation. As a result, the TmNiAl₂ compound shows the largest $(-\Delta S_M)_{max}$. Though the TmNiAl₂ compound has been proved to have two magnetic transition temperatures, no double peaks were observed on the $(-\Delta S_M)$ curves because two transition temperatures are too much close and the contributions of two magnetic transitions mix together. According to the ΔS_M curves, the temperature windows of cooling for the TmNiAl₂ compound are 2.2 K–9.3 K and 2.4 K–18.0 K for field changes of 0–2 T and 0–5 T, respectively. The working temperature range completely covers the liquid helium boiling point of 4.2 K. It is noteworthy that the inverse MCE is observed below 10 K for the TbNiAl₂ compound. To be specific, the value of $-\Delta S_M$ is calculated to be -1.1 J/kg K and -0.3 J/kg K at 5.2 K and 7.0 K, respectively, under a field change of 0–2 T. The negative value of $-\Delta S_M$ indicates an inverse magnetocaloric effect. It resulted from the AFM contribution in FIM ground state at low temperatures. The inverse MCE has been observed in many kinds of MCE materials with AFM ground state.³¹ For the GdNiAl₂ compound, no sharp decrease of $(-\Delta S_M)$ can be observed when the



FIG. 8. Rescaled universal curves for applied magnetic fields from 1 up to 5 T for RNiAl₂ (R = Tm, Tb, and Gd) compounds.



FIG. 9. Dependence of the magnetic entropy change on the parameter $(\mu_0 {\rm H})^{2/3}$ for RNiAl_2 (R = Tm, Tb, and Gd) compounds.

temperature decreases from T_C to lower temperatures. It keeps a relatively high value in the temperature range between around 10 K and 30 K, which is in agreement with a previous work.²⁴ The performance of magnetic entropy change curves is related to the magnetic transition of the GdNiAl₂ compound. From Fig. 3(c), it can be clearly seen that except for a sharp change of the M-T curve around T_C, there is also a relatively gentle change at lower temperatures. This gentle change of the M-T curve has been observed in the GdNiAl₂ compound before.²⁴ Actually, this kind of change of magnetization observed below T_C is similar to spin reorientation transition, where the easy axis changes continuously with decreasing temperature due to the competition between magnetic exchange interaction and magnetocrystalline anisotropy, such as DyGa and TbGa compounds.³² However, the GdNiAl₂ compound is still described as the FM material due to the lack of evidence of magnetic structural changes at low temperatures, which is in accordance with the description presented in previous report.²

Figure 7 presents the Arrott plots M² vs H/M of RNiAl₂ compounds derived from M-H curves. According to Banerjee's criterion, the magnetic transition is of the second order for a positive slope; otherwise, it is of the first order.³³ For the TmNiAl₂ compound, the slope of the Arrott plots at 2.2 K is negative, resulting from the field-induced two-stage magnetic transition. The transition type around T_C is still of the second order according to the positive slopes of Arrott plots. For the TbNiAl₂ compound, the slopes of the curves are negative below 20 K resulting from the AFM to FM transition, but they change to be positive at the temperatures above T_C. It indicates that the phase transition around T_C is of the second order. For the GdNiAl₂ compound, all curves show a monotonic increase with positive slopes, indicating a secondorder magnetic transition. Actually, the good thermal reversibility based on ZFC and FC curves can also be considered an evidence of a second-order magnetic transition for $RNiAl_2$ (R = Tm, Tb, Gd) compounds, because obvious and large thermal hysteresis would always be observed in the MCE materials of the first-order magnetic transition, such as Ni-Mn-In-(Co).⁷ To further confirm the type of magnetic transitions, rescaled universal curve and mean field theory criteria were also used to provide evidence.

The rescaled universal curves are shown in Fig. 8. For TmNiAl₂, TbNiAl₂, and GdNiAl₂ compounds, the normalized and rescaled experimental ΔS_M curves for different applied magnetic fields collapse into a universal curve, indicating the presence of a secondorder phase transition. The results from mean field theory criteria are shown in Fig. 9. For the TmNiAl₂ compound, $|\Delta S_M|$ as a function of $H^{2/3}$ around T_C shows an obvious deviation from the linear relationship, indicating a first-order transition. For the $TbNiAl_2$ compound, $|\Delta S_M|$ as a function of $H^{2/3}$ around T_N exhibits a slight deviation from the linear relationship. However, it cannot be taken as the evidence of a first-order transition, because the magnetic state is AFM rather than FM. For the GdNiAl₂ compound, it is a second-order transition because $|\Delta S_M|$ as a function of $H^{2/3}$ around T_C shows a well linear relationship. Based on the above results and discussion, it indicates that GdNiAl₂ and TbNiAl₂ compounds are of a second-order phase transition while the TmNiAl₂ compound is a mixture of the first- and second-order transitions.

The refrigeration capacity (RC) is also an important parameter to evaluate the performance of MCE materials. There are three methods to calculate RC: (1) It is calculated by $RC-1 = \int_{T_1}^{T_2} |\Delta S_M(T, H)| dT$, where T_1 and T_2 are the temperature corresponding to both sides of the half maximum value of the $-\Delta S_{\rm M}$ peak, respectively.³² (2) It is defined as the product of $(-\Delta S_M)_{max}$ and the full width at half maximum in the ΔS_M (T) curve (coincides with the temperature span of the thermodynamic cycle, $\delta T_{FWHM} = T_2 - T_1$). RC-2 = $(-\Delta S_M)_{max} \times \delta T_{FWHM}$.³⁴ (3) It is determined by maximizing the product of $-\Delta S_{\rm M}$ and the corresponding δT in the $\Delta S_M(T)$ curve and marked as RC-3.³⁵ The RC-1 calculated from the first method was used more generally. The value of RC-1 is calculated to be 74.4, 101.5, and 183.0 J/kg under the field change of 0-2 T for TmNiAl₂, TbNiAl₂, and GdNiAl₂, respectively. The value of RC-1 under the field change of 0-5 T is calculated to be 245.7, 296.5, and 502.9 J/kg for TmNiAl₂, TbNiAl₂, and GdNiAl₂, respectively. To compare the MCE performance between RNiAl₂ series and other MCE materials with a similar working temperature zone, magnetic parameters including RC-1, RC-2, RC-3, and $\delta T_{\rm FWHM}$ are all listed in Table II. The results of the GdNiAl₂ compound are in accordance with previous

TABLE II. Magnetocaloric properties of RNiAl2 and some representative refrigerant materials with magnetic transition temperatures.

Samples	T _{ord} (K)	$-\Delta S_{\rm M}$ (J/kg K)		δT _{FWHM} (K)		RC-1 (J/kg)		RC-2 (J/kg)		RC-3 (J/kg)		
		0–2 T	0–5 T	0–2 T	0–5 T	0–2 T	0–5 T	0–2 T	0–5 T	0–2 T	0–5 T	References
TmNiAl ₂	2.4/4.0	14.5	20.7	7.3	15.6	74.4	245.7	76.0	322.6		160.2	This work
TbNiAl ₂	11.0/21.5	6.8	11.8	18.4	32.0	101.5	296.5	125.1	379.7	109.8	190.2	This work
GdNiAl ₂	30.5	9.4	17.3	35.4	38.7	183.0	502.9	328.9	668.3	145.2	339.5	This work
GdNiAl ₂	28.0		16.0				507.5 ^ª		640.0			24
HoNiAl ₂	7.8	9.7 ^a	14.0			54.0	171.0	84.0	213.0			26
ErNiAl ₂	5.1	11.8 ^a	21.2			104.0	267.0	137.0	357.0			26
Gd _{0.1} Er _{0.9} Ga	20.6/49.0	4.8	11.4			184.7	535.2	233.3	640.7			27
Ho ₀ ₁ Er ₀ ₉ Ni	9.0/11.0	18.0	34.0			104.2	366.6	126.0	482.8			28
ErMn ₂ Si ₂	4.5	20.0	25.2			93.4 ^a	252.3 ^a	130.0	365.0			36
TmZn	8.0	19.6	26.9			61.0	211.5	76.0	269.0			19

^aThese results are estimated from the relevant references.

reports.²⁴ Among the RNiAl₂ compounds, ErNiAl₂ and TmNiAl₂ compounds exhibit a much larger $(-\Delta S_M)_{max}$ and the GdNiAl₂ compound shows a much larger RC-1 value.²⁴ The good performance of RC-1 for GdNiAl₂ results from the gentle change of magnetization with temperature in the low temperature range, and the magnetic entropy change decreases slowly with the temperature decreasing from T_C. Among MCE materials in the low temperature range, the Gd_{0.1}Er_{0.9}Ga compound shows a much larger RC-1 but $(-\Delta S_M)_{max}$ value is unfortunately not high.²⁷ Ho_{0.1}Er_{0.9}Ni, $ErMn_2Si_2,$ and TmZn compounds show larger values of $(-\Delta S_M)_{max}$ but with moderate RC-1 values.^{19,28,36} Based on the data in Table II, the GdNiAl₂ compound shows relatively high values of $(-\Delta S_M)_{max}$ and RC-1. Therefore, for overall considerations, the MCE performance of the GdNiAl₂ compound is comparably good. A large $(-\Delta S_M)$ was observed for the TmNiAl₂ compound around the liquid helium boiling point, indicating that TmNiAl₂ materials have potential applications in low-temperature magnetic refrigeration.

IV. CONCLUSION

The magnetic properties and MCEs of RNiAl₂ (R = Tm, Tb, Gd) compounds were investigated in detail. For the TmNiAl₂ compound, FM-FM transition and FM-PM transition were observed at very low temperatures of 2.4 K and 4.0 K, respectively. The TbNiAl₂ compound undergoes an FIM to AFM transition and an AFM to PM transition at 11.0 K and 21.5 K, respectively. As the temperature increases, the GdNiAl₂ compound undergoes an FM to PM transition at 30.5 K. For the magnetic field change of 0–5 T, the values of $(-\Delta S_M)_{max}$ and RC-1 are calculated to be 20.7, 11.8, and 17.3 J/kg K and 245.7, 296.5, and 502.9 J/kg for TmNiAl₂, TbNiAl₂, and GdNiAl₂, respectively. The large MCE and low working temperatures near the liquid helium boiling point make RNiAl₂ compounds competitive among low-temperature MCE materials.

ACKNOWLEDGMENTS

This work was supported by the National Key Research and Development Program of China (No. 2017YFB0702701), the National Natural Science Foundation of China (NNSFC) (Nos. 51871019, 11674008, 51625101, 51431009, and 51590881), the National Basic Research Program of China (Nos. 2015CB921401), Key Program of the Chinese Academy of Sciences (No. 112111KYSB20180013), and the Fundamental Research Funds for the Central Universities (No. FRF-TP-16-001C2).

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