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Nearly constant magnetic entropy change and adiabatic temperature change in PrGa compound

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The magnetic properties and magnetocaloric effect (MCE) of PrGa compound are studied in detail. Both thermomagnetization curves and heat capacity curves indicate that PrGa compound undergoes a transition from ferromagnetic (FM) to antiferromagnetic (AFM) phase at $T_t \sim 27$ K and a transition from AFM to paramagnetic (PM) phase at $T_0 \sim 37$ K with increasing temperature. As the applied field increases, the magnetic state between T_t and T_0 shows an obvious metamagnetic transition from AFM to FM state. The magnetic entropy change (ΔS_M) calculated from magnetic property measurement and that obtained from heat capacity measurement are in good agreement with each other above 25 K. Instead of peak like distribution, nearly constant value of ΔS_M in a temperature range from 29.5 K to 37.5 K is observed when the field change is 0–5 T. The adiabatic temperature change (ΔT) also shows similar change rules. This characteristic of MCE is very important for the practical applications of magnetic refrigerant materials. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4868203]

I. INTRODUCTION

Magnetic refrigeration has attracted much attention for its high efficiency and environmental friendliness compared with conventional gas compression-expansion refrigeration.[1–3] Magnetic refrigeration is based on magnetocaloric effect (MCE), and the materials used for magnetic refrigeration are mainly evaluated by two important parameters: isothermal magnetic entropy change (ΔS_M) and adiabatic temperature change (ΔT).[4] Lots of materials with large ΔS_M near room temperature have been found 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.[5–10] And many materials showing large ΔS_M in low temperature range have also been studied, as they can be used for gas liquefaction.[11–14] In most cases, the curves of ΔS_M or ΔT are peak like distribution and platforms can be observed only for certain materials near room temperature region such as $LaFe_{11.8}Si_{1.2}$ and $LaFe_{11.44}Al_{1.56}$.[15,16] The feature of nearly constant ΔS_M or ΔT in a wide temperature range is very important for practical applications of materials. However, hardly any material with such a characteristic has been found in low temperature zone.

Binary intermetallic compounds between rare earth and gallium show interesting magnetic properties in middle and low temperature zones. And most of them undergo a spin reorientation transition (SR) and a ferromagnetic (FM)-to-paramagnetic (PM) transition in sequence with increasing temperature.[14,17–20] According to previous work, PrGa compound undergoes an FM-to-antiferromagnetic (AFM) transition at 28 K and an AFM-to-PM transition at 36 K with increasing temperature. Obvious magnetostriction and large magnetoresistance are observed between 28 K and 36 K.[21] Another interesting result is that the transition in lower temperature zone is different from those other RGa compounds.[14,18–20] In this work, we study the properties of PrGa compound in detail and calculate the MCE by two methods. Considering the fact that the relevant data of PrGa in Ref. 21 are neither complete nor detailed, the magnetization and heat capacity data are all measured in this paper.

II. EXPERIMENTAL DETAILS

The PrGa compound was prepared with arc-melting furnace. First, Pr and Ga were poured together by an atom ratio of 1:1 and the purity of the starting elements is more than 99.9%. Second, they were melted in argon atmosphere and formed an ingot. Third, the ingot was wrapped with the molybdenum foil and placed into a quartz tube which was in high-vacuum state. Then the tube was located into a box resistor-stove and kept there for a week at 1073 K. Finally, the quartz tube was quenched in liquid nitrogen and smashed. When the liquid nitrogen evaporated, PrGa sample was ready. The phase purity and crystal structure of PrGa were confirmed by powder X-ray diffraction (XRD). The primary magnetic property was obtained by Quantum-Designed Vibrating Sample Magnetometer (SQUID-VSM). The transport property was obtained by heat capacity measurements on Physical Property Measurement System (PPMS). Especially, the thermal magnetization curves are zero-field cooled and measured with increasing temperature. The isothermal magnetization curves are measured with field

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increasing and the heat capacity curves are measured with increasing temperature. Then the ΔS_M was calculated from *M–H* data and C_H–*T* data, respectively. The value of ΔT was also obtained from the above data.

III. RESULTS AND DISCUSSION

The room temperature XRD pattern of PrGa is obtained, and all of the peaks can correspond to the Bragg positions of Cr-B type crystal structure. The space group of the sample is *Cmcm* (#63), which is the same as those previously reported.[22,23] The fact that no impurity peaks are observed confirms the single-phase feature of PrGa compound.

To study the magnetic properties of PrGa, thermomagnetization and heat capacity curves at different magnetic fields are measured (not shown here). From *M–T* curves at 0.05 T, we can see that the magnetization curve experiences two drops at 27 K and 37 K, respectively. The sharp changes are corresponding to two magnetic transition temperatures marked as T_t and T_0. The transition at lower temperature is considered to be the FM-to-AFM transition reported by Chen *et al.*[21] The transition at higher temperature is AFM to PM transition and the value of T_0 is in good accordance with reported results.[17,21] As the applied field is added, T_t moves to higher temperature zone. When the applied field is high enough, metamagnetic transition occurs in the whole temperature region between T_t and T_0, thus the two drops of magnetization almost become one. The *M-T* curves of PrGa are very similar to those of $LaFe_{11.44}Al_{1.56}$.[16]

The heat capacity results (not shown here) show similar change rules with *M–T* curves. Two peaks are clearly shown on the C_H–*T* curve when the applied field is zero. And the two peaks are corresponding to T_t and T_0, respectively. The peak at lower temperature moves toward higher zone with increasing applied field. When the applied filed exceeds a certain value, the two peaks turn into a large one, such as those in the case of 1, 2, and 5 T. In fact, the performance of C_H-*T* curve is the inevitable result of thermomagnetization data. The magnetic contribution to heat capacity can be expressed as $C_H = -(H_e + \alpha M) * \frac{\partial M}{\partial T}$ according to Ref. 18 and 24, where He is the external field. According to this formula, a sudden drop of magnetic moment on the *M–T* curve can definitely cause a sharp peak on the C_H–*T* curve. As a result, obvious peaks are observed on C_H–*T* curves near T_t and T_0.

To confirm the ground state of each temperature range and the type of magnetic transitions, isothermal magnetizations up to 5 T in a temperature range from 11 K to 75 K are measured in detail (see Fig. 1). From Fig. 1, we can see that magnetic moments reach saturation values quickly with increasing magnetic field below 27 K, which indicates the FM ground state. As for the temperatures between T_t and T_0, the magnetization curve shows a linear increase and then a sudden jump with increasing magnetic field, which appears to indicate the metamagnetic transition from AFM to FM phase.[16] The critical field of metamagnetic transition from AFM to FM state determined by the maximum value of $\partial M/\partial T$ is also calculated. The result indicates that the critical field increases with increasing temperature. In other words, the temperature zone where metamagnetic transition

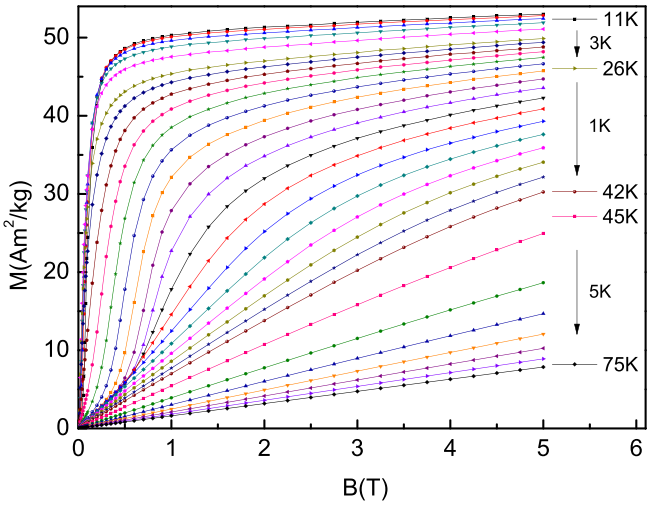

FIG. 1. Isothermal magnetization curves up to 5 T in temperature ranges of 11 K–75 K.

happens extends with increasing applied field. It is consistent with the conclusion obtained from *M–T* curve. Besides, the Arrott plots indicate that the field-induced metamagnetic transition between T_t and T_0 is of first order, and it is related to the volume transition there.[25] And that the transition temperature moves to higher zone is the important characteristic of first order transition.[26] The magnetic property mentioned above has an important effect on MCE.

The value of ΔS_M is calculated from magnetization data according to the Maxwell relation $\Delta S_M = \int_0^H (\frac{\partial M}{\partial T})_H dH$. It should be noted that deviations may exist between the obtained value and the true one, because the hysteresis is not taken into account. The value of ΔS_M is also calculated from heat capacity data and the ΔS_M–*T* curves obtained from the two methods are shown in Fig. 2(a). We know that there is a standard method to extract ΔS_M from C_H data.[27] However, we need to make some modifications to that method, for the starting temperature of heat capacity measurement for PrGa compounds is not so idealized as 0 K. The key point of modification is to replace the reference temperature of 0 K with 72.5 K.

In this case, the value of $\Delta S_M(72.5K)_{0-5T}$ is not zero, but we can acquire its value from the calculations of *M-H* data. The reason why we choose 72.5 K as the reference temperature is that the magnetic ground state and magnetic transition are clearly known here far from T_0. And we can see that the curves obtained from the two methods are consistent well with each other above 25 K. Large deviation below 25 K may result from the complex magnetic structure and magnetic transition in PrGa compound. The adiabatic ΔT (Fig. 2(b)) is obtained in the method suggested by Pecharsky and Gschneidner[4] and it is summarized below. First, $S(T)_{0T}$ is obtained from heat capacity data and $S(72.5\,K)_{0T}$ is set to be zero. Second, $S(T)_{5T}$ is obtained from $S(T)_{0T}$ and $\Delta S_{M,0\text{-}5T}$, which is calculated from *M–H* data. Third, we can obtain the curves of $T(S)_{0T}$ and $T(S)_{5T}$, which are the inverse functions of $S(T)_{0T}$ and $S(T)_{5T}$, respectively. Finally, we make a difference according to the formula $T(S)_{5T}$–$T(S)_{0T}$ and then the ΔT–*T* curves are obtained.

As two most important parameters to characterize MCE, ΔT and ΔS_M curves show similar change rules according to

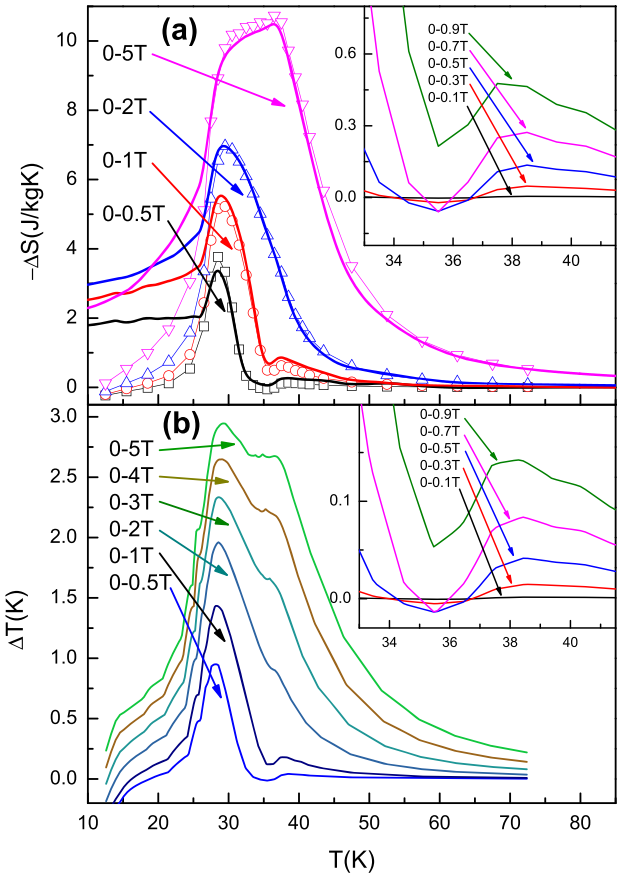

FIG. 2. (a) Magnetic entropy change curves obtained from heat capacity measurement (solid lines) and magnetic property measurement (empty symbols). The inset shows the curves for low fields obtained from magnetic property measurement. (b) Adiabatic temperature change curves for an applied field of 0.5, 1, 2, 3, 4, and 5 T. The inset is the relevant curves for low fields.

Figs. 2(a) and 2(b). When the magnetic field change is small, such as 0.05 T and 1 T, two peaks are observed on the curves near T_t and T_0, respectively. That is to say, both the field-induced AFM-to-FM transition and field-induced PM-to-FM transition contribute to MCE. We can also see that the peak near T_t is much higher than that near T_0. That is because the AFM to FM transition is of first order and accompanied by volume transition, which always plays an important role in enhancing MCE.[11,15] With increasing field change, the peak in lower temperature zone shifts towards higher temperature region. When the field change is high enough such as 5 T, the two peaks are merged together and a wide platform is observed on the curve from 29.5 K to 37.5 K. This kind of material with nearly constant ΔT and ΔS_M in a wide temperature range has many practical applications, because people can use as few materials as possible in the limited space of magnetic refrigerator to realize refrigeration. The magnetic property and MCE of PrGa are very similar to those of $LaFe_{11.44}Al_{1.56}$.[16] Some other RGa compounds have the same crystal structures as PrGa compounds, but no platforms are found on their ΔS_M–T curves.[14,19,20] The main difference is that the magnetic transition at lower temperature is FM-to-FM transition and the transition temperature does not shift toward higher zone obviously with increasing applied field for other RGa compounds.[14,19,20] Though the maximum value of ΔS_M and ΔT for PrGa is not large enough ($(\Delta S_M)_{max}$ is 10.7 J/kg K and $(\Delta T)_{max}$ is 2.9 K for a field change of 5 T), the feature of nearly constant ΔS_M and ΔT is valuable for researches compared with other RGa compounds. This feature of MCE is very important for practical applications of magnetic refrigerant materials. This work is instructive to explore and research refrigerant materials in low temperature zone. Anyway, the future work is still necessary to improve the maximum value of ΔS_M and keep the platform on the curves at the same time. The ΔS_M and ΔT curves for small field change are also shown in the insets of Figs. 2(a) and 2(b), respectively. The small peaks caused by the field-induced PM-to-FM transition are clear when the field change is small. Positive ΔS_M value and negative ΔT value are observed around 35.5 K for the field changes of 0.1, 0.3, and 0.5 T, because the field change is so small that the metamagnetic transition cannot happen. And similar results in AFM ground state materials have been reported more than once.[27,28]

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[1]A. M. Tishin and Y. I. Spichkin, in *The Magnetocaloric Effect and its Applications*, edited by J. M. D. Coey, D. R. Tilley, and D. R. Vij (Institute of Physics, London, 2003).
[2]V. K. Pecharsky and K. A. Gschneidner, Jr., J. Magn. Magn. Mater. **200**, 44 (1999).
[3]B. G. Shen *et al.*, Adv. Mater. **21**, 4545 (2009).
[4]V. K. Pecharsky and K. A. Gschneidner, Jr., J. Appl. Phys. **86**, 565 (1999).
[5]V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).
[6]H. Wada and Y. Tanabe, Appl. Phys. Lett. **79**, 3302 (2001).
[7]O. Tegus *et al.*, Nature (London) **415**, 150 (2002).
[8]F. X. Hu *et al.*, Appl. Phys. Lett. **78**, 3675 (2001).
[9]B. G. Shen *et al.*, Chin. Phys. B **22**, 017502 (2013).
[10]F. X. Hu *et al.*, Appl. Phys. Lett. **76**, 3460 (2000).
[11]J. D. Zou *et al.*, Chin. Phys. B **16**, 1817 (2007).
[12]N. K. Singh *et al.*, J. Appl. Phys. **101**, 093904 (2007).
[13]X. Q. Zheng *et al.*, Appl. Phys. Lett. **102**, 022421 (2013).
[14]J. Chen *et al.*, Appl. Phys. Lett. **95**, 132504 (2009).
[15]S. Fujieda *et al.*, Appl. Phys. Lett. **81**, 1276 (2002).
[16]F. X. Hu *et al.*, IEEE Trans. Magn. **37**, 2328 (2001).
[17]N. Delyagin *et al.*, J. Magn. Magn. Mater. **308**, 74 (2007).
[18]J. Y. Zhang *et al.*, J. Alloys Compd. **469**, 15 (2009).
[19]J. Chen *et al.*, Solid State Commun. **150**, 157 (2010).
[20]X. Q. Zheng *et al.*, J. Appl. Phys. **111**, 07A917 (2012).
[21]J. Chen *et al.*, Appl. Phys. Lett. **99**, 122503 (2011).
[22]K. H. J. Buschow, Rep. Prog. Phys. **42**, 1373 (1979).
[23]N. Shohata, J. Phys. Soc. Jpn. **42**, 1873 (1977).
[24]A. R. Dinesen *et al.*, J. Magn. Magn. Mater. **253**, 28 (2002).
[25]A. Fujita and K. Fukamichi, IEEE Trans. Magn. **35**, 3796 (1999).
[26]A. Fujita *et al.*, Phys. Rev. B **67**, 104416 (2003).
[27]T. Samanta *et al.*, Appl. Phys. Lett. **91**, 152506 (2007).
[28]J. Shen *et al.*, Appl. Phys. A **99**, 853 (2010).