Magnetocaloric properties in the $PrFe_2Ge_2$ antiferromagnet

Zhi-Yi Xu*, Wen-Jie Gong, and An-Li Lin
National Institute of Metrology,
Beijing 100029,
China
zhyxu@nim.ac.cn

Yan Zhang,
Department of Physics,
Capital Normal University, Beijing 100048,
China

Li-Cheng Wang and Yan Zhang
Institute of Physics,
Chinese Academy of Sciences, Beijing 100190,
China

***Abstract*— Magnetic properties and magnetocaloric effects (MCE) of the tetragonal ($ThCr_2Si_2$-type) $PrFe_2Ge_2$ compound are investigated. The compound is determined to be antiferromagnet with the Néel temperature T_N=14.5 K and undergoes a transition towards an incommensurate modulated structure at 7 K. A field-induced metamagnetic transition from antiferromagnetic (AFM) to ferromagnetic (FM) state occurs at 5 K under the critical magnetic field of 11 kOe. The maximum values of magnetic entropy change (ΔS) are –1.1 J/kg K and –6.3 J/kg K for the field changes of 0-20 kOe and 0-70 kOe, respectively. The large MCE with no hysteresis loss renders $PrFe_2Ge_2$ a competitive candidate for low temperature magnetic refrigerant.**

Keywords*— *$PrFe_2Ge_2$; antiferromagnet; metamagnetic transition; magnetocaloric effect

I. INTRODUCTION

Nowadays, the economy is booming up and puting much pressure to the environment. For this reason, a lot of attention has been paid to the research on biology and environment protection. Recently, magnetocaloric effect (MCE) technology is considered to be prospective in the refrigeration regime due to its merits of high energy-efficiency and eco-friendly characteristics in comparison with traditional gas-compression refrigeration [1-4]. The application of room temperature magnetic refrigeration could significantly reduce the emission of green-house gas. Since the first discovery of giant MCE in $Gd_5Si_2Ge_2$ [5], a great number of magnetic materials with excellent performance around room temperature such as La(Fe, Si)$_{13}$ [6], $MnA_{s1-x}Sb_x$ [7], $MnFeP_{1-x}As_x$ [8] and NiMn-based Heusler alloys [9] have been reported and studied extensively in the past decades. On the other hand, the materials with large MCE in low temperature regime are suitable for the gas liquifaction and could help cryogenic facility to reach mili-kelvin [10]. Up to now, some paramagnetic salts with the rare-earth element such as $Gd_3Gd_5O_{12}$, $GdLiF_4$ or GdF_3 have been commercially employed [11]. However, the MCE of most paramagnetic salts is relatively low, which restrains the application of paramagnetic salts. In recent years, rare earth-transition metal intermetallic compounds with ferromagnetic (FM) to paramagnetic (PM) transition or antiferromagnetic (AFM) to FM metamagnetic transition are extensively investigated due to their large MCE in comparison with that of paramagnetic salts [12, 13].

Generally, the magnetic refrigeration can be realized via the variation of the magnetic field, and the magnitude of MCE is characterized by the isothermal magnetic entropy change and/or the adiabatic temperature change [1-10]. The susceptibility [14] and specific heat [15] of $PrFe_2Ge_2$ have been reported in previous papers. In this paper, we further studied the magnetic and MCE properties of $PrFe_2Ge_2$, and found a large ΔS without hysteresis loss in low temperature range (around 14.5 K), making $PrFe_2Ge_2$ a potential refrigerant in low.

II. MATERIALS AND METHOD

The $PrFe_2Ge_2$ ingot was prepared by arc melting method with the stoichiometric starting materials (Pr, Fe and Ge) on a water-cooled copper crucible under the protection of high-purity argon atmosphere. The purity of all constituents are better than 99.9 wt.%.Considering the volatility, 2 wt.% excess Pr was added to compensate for the evaporation losses during the arc melting. Before the melting, all the crude materials were polished and subsequently washed in ultrasonic cleaner to clean the oxide coating on the surface of metals. The sample was turned over and remelted for several times to ensure the homogeneity. The resulting ingot was sealed in a quartz tube fulfilled with high-purity argon atmosphere and then annealed at 1173 K for 2 weeks. Powder X-ray diffractometer (XRD) from Bruker Inc by using Cu Kα radiation was employed to determine the lattice parameter and phase composition of the final product. The magnetic measurement was performed on a commercial SQUID from Quantum Design by using a small piece of the sample.

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III. Results and Discussion

Fig. 1 shows the powder XRD patterns for $PrFe_2Ge_2$ sample collected at room temperature. It reveals that all the peaks can be indexed according to the PDF data base (PDF#65-5579), and thus the sample is determined to crystallize in a pure phase tetragonal $ThCr_2Si_2$-type structure (space group: I4/mmm, No. 139) as reported before [14, 16]. Within the margin of experimental error, the lattice parameters *a* and *c* are determined to be 4.063 and 10.542 Å respectively, which are in a good agreement with the published results in [14] and [16].

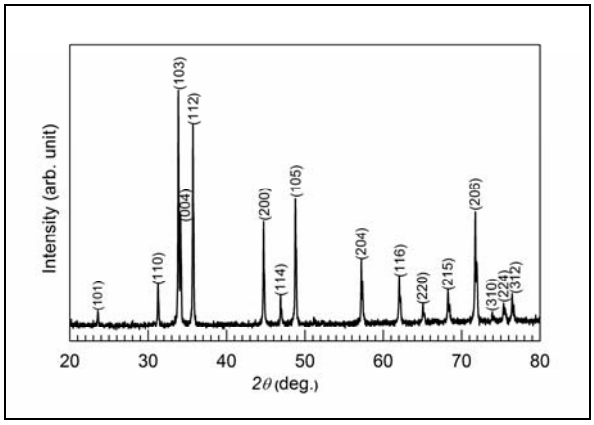

Fig. 1. XRD spectrum for the $PrFe_2Ge_2$ compound.

Fig. 2 displays the temperature (*T*) dependence of both zero-field cooling (ZFC) and field-cooling (FC) magnetizations (*M*) under a magnetic field of 0.1 kOe. A λ-type peak around 14.5 K can be clearly seen in both ZFC and FC branchs, which is considered to be a feature of AFM-PM transition. It has been reported that $PrFe_2Ge_2$ exhibits an AFM ground state with the transition Néel temperature T_N around 14.5 K [14, 15], consistent with the result of our work. On the other hand, a transition at 7 K is detected, which is close to the transition towards an incommensurate modulated structure at 9 K as published before [14]. The peculiar magnetic behavior of $PrFe_2Ge_2$ between the two transition temperatures was extensively researched and was considered as a progressive squaring of the sine modulation of the Pr moments which would take place in this range of temperature [14, 15]. The reciprocal susceptibility ($1/\chi$) under ZFC mode as a function of temperature obtained at 0.1 kOe is plotted in the inset of Fig. 2. It can be seen that the $1/\chi$ obeys the Curie-Weiss law in the PM region with an effective magnetic moment $\mu_{eff} = 4.80\ \mu_B$, which is larger than the free ion value of Pr^{3+} (3.58 μ_B), implying the possible presence of Fe moment. On the other hand, the paramagnetic Curie temperature (θ_p) derived from the Curie-Weiss fit in the paramagnetic span is –8.8 K. This negative value of θ_p further confirms the antiferromagnetic ordering in $PrFe_2Ge_2$ compound.

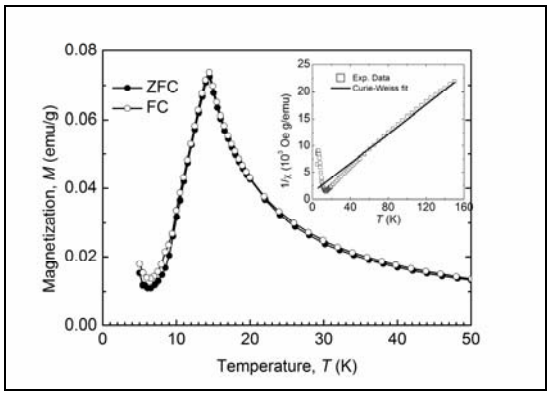

Fig. 2. Temperature dependences of magnetization measured in ZFC and FC modes for $PrFe_2Ge_2$ compound. The inset displays the temperature variation of the inverse susceptibility fitted to the Curie-Weiss law.

Fig. 3 exhibits the initial magnetization curves in a temperature range of 5-15 K under the magnetic fields up to 70 kOe, with the inset showing the magnetic hysteresis loop at 5 K. The magnetic hysteresis loop at 5 K shows a negligible hysteresis effect, which could reduce the energy loss in practical application of magnetic refrigerant during the cyclic variation of magnetic field and increase the coefficient of utilization. The crossover among the curves and a clear change in the slope of the curve at 5 K indicate a field-induced metamagnetic transition from AFM to FM states with a critical field of 11 kOe, coincide with the earlier report [14]. In addition, the magnetization curve at 5 K shows a tendency of saturation with the increase of magnetic field, and reaches a maximum magnetization of 2.08 μ_B under 50 kOe.

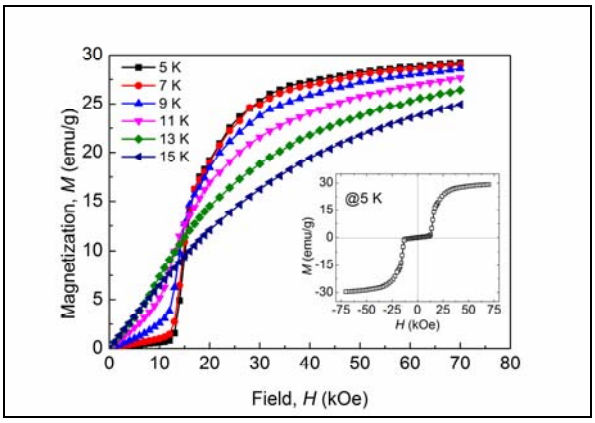

Fig. 3. Initial isothermal magnetization curve at typical temperatures, with the inset showing the magnetic hysteresis loop at 5 K up to 70 kOe.

The isothermal magnetization curves (*M-H*) measured in a heating mode under applied fields up to 70 kOe are shown in Fig. 4(a). Fig. 4(b) presents the Arrott-plots (M^2 vs H/M), derived from *M-H* isotherms in Fig. 4(a), for $PrFe_2Ge_2$ compound measured at typical temperatures. The negative slope of the Arrott plots below T_N as presented in Fig. 4(b) confirms the occurrence of a first order AFM-FM phase transition according to the Banerjee criterion [17].

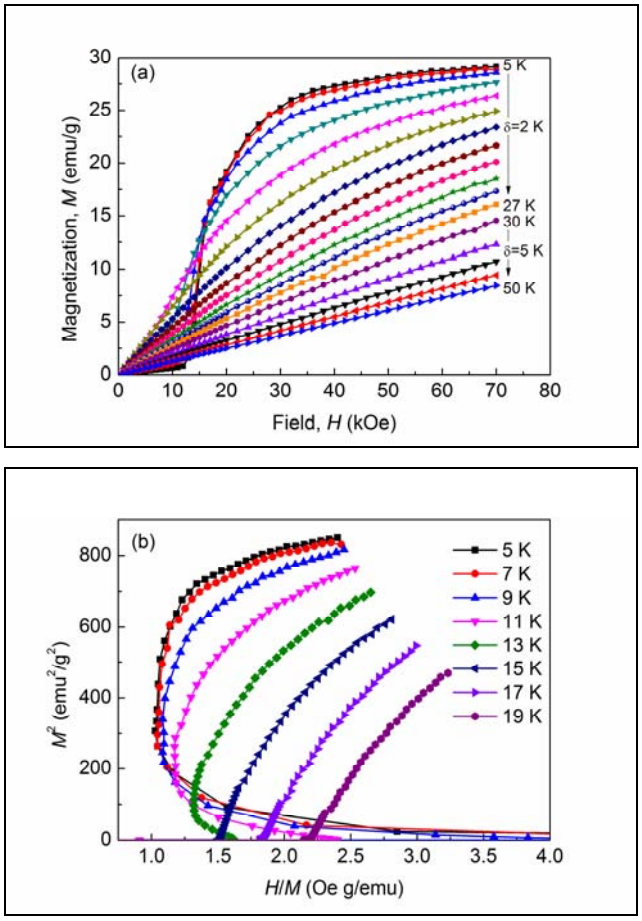

Fig. 4. An example of a figure caption. Magnetic isothermals (a) and Arrott-plots (b) of $PrFe_2Ge_2$ measured during field increasing.

The isothermal magnetic entropy change was calculated from the isothermal magnetization data by employing Maxwell relationship [10]:

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

The ΔS as a function of temperature (ΔS-T) for different magnetic field changes are shown in Fig. 5. It can be seen from Fig. 5 that the $PrFe_2Ge_2$ shows a ΔS peak around T_N, and the maximum values of ΔS are found to be –1.1 J/kg K and –6.3 J/kg K for the field changes of 0-20 kOe and 0-70 kOe, which are comparable with other popularly researched magnetic refrigerant materials, such as, $GdPd_2Si$ (–8.6 J/kg K) [18], and RNi_5 (–8 J/kg K) [19] in low temperature regime under the same field changes. The positive values of ΔS observed in low temperature range are attributed to the presence of AFM nature below T_N. The large ΔS without hysteresis loss as well as low T_N make $PrFe_2Ge_2$ a potential candidate of low temperature magnetic refrigerants.

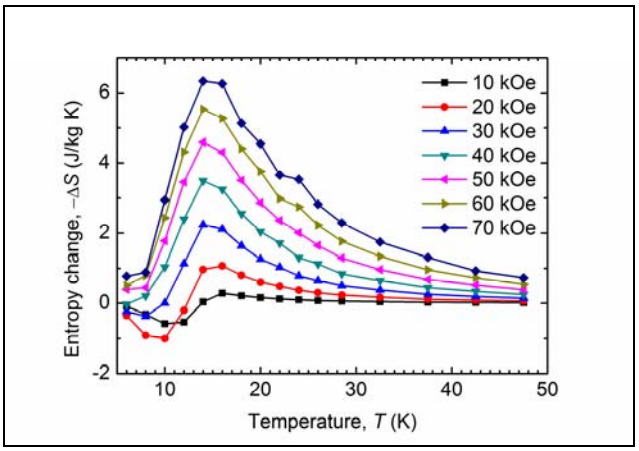

Fig. 5. Example of a figure caption. Magnetic entropy changes as a function of temperature for $PrFe_2Ge_2$ compound under various magnetic field changes up to 70 kOe.

IV. CONCLUSIONS

In summary, the magnetic and MCE properties of $ThCr_2Si_2$-type structure $PrFe_2Ge_2$ have been investigated. The ground state of the sample is determined to be AFM with T_N =14.5 K and a field-induced metamagnetic transition from AFM to FM states below T_N occurs at 5 K under an applied magnetic field of 11 kOe. Large MCE without magnetic hysteresis loss is observed due to the field-induced metamagnetic transition. The maximum values of magnetic entropy change (ΔS) are found to be –1.1 J/kg K and –6.3 J/kg K for the field changes of 0-20 kOe and 0-70 kOe, respectively. The merits of large ΔS together with no hysteresis loss as well as low T_N make $PrFe_2Ge_2$ a competitive candidate as low temperature magnetic refrigerant.

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