Reversible room-temperature magnetocaloric effect in Mn$_5$PB$_2$

Z. G. Xie,[a)] D. Y. Geng, and Z. D. Zhang
Shenyang National Laboratory for Materials Science, Institute of Metal Research, and International Centre for Materials Physics, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, People's Republic of China

Magnetic properties and magnetocaloric effect of the Mn$_5$PB$_2$ compound have been investigated. The maximum values of magnetic entropy change $-\Delta S_M$ at 302 K are 4.93 and 2.64 J kg^{-1} K^{-1} for magnetic field changes of 5 and 2 T, respectively, which are closely related with a second-order magnetic transition from the ferromagnetic to the paramagnetic state. The reversible magnetocaloric effect with relatively large magnetic entropy change makes the Mn$_5$PB$_2$ compound (free of rare earths) and Mn$_5$PB$_2$-based materials attractive candidates for room-temperature magnetic refrigeration. © 2010 American Institute of Physics. [doi:10.1063/1.3518064]

The magnetic refrigeration based on magnetocaloric effect (MCE) has attracted a great deal of interest for its energy-efficient and environment-friendly behavior, compared to the common vapor-cycle refrigeration technology.[1–4] In particular, much attention has been paid to development of technologies for room-temperature magnetic refrigeration.[4–15] Because considerable thermal and magnetic hysteresis induced by the first-order magnetic transition (FOMT) would confine practical applications of giant-MCE materials,[4–7] recently, a lot of work focused on searching magnetic refrigerant materials with a large reversible MCE based on a second-order magnetic transition (SOMT).[16–18] However, the main challenge in the field of room-temperature magnetic refrigeration is still to realize large and reversible magnetic entropy changes at/near room-temperature, without thermal and magnetic hysteresis, at magnetic fields as smaller as possible.

On the other hand, in general, the cost of MCE materials based on magnetic 3d elements is much cheaper than that of ones based on rare earth elements. Consequently, it is of great importance to explore new compounds free of rare earths, which exhibit large entropy changes with a SOMT near room-temperature. Magnetic properties and MCE of several Mn-based compounds, such as MnFeP$_{0.45}$As$_{0.55}$,[4] Mn$_{1-x}$Cr$_x$As,[6] Ni–Mn–X (X=In,Sb,Sn,Ga),[12–15,19] Mn$_3$GaC,[20] ε-(Mn$_{0.83}$Fe$_{0.17}$)$_{3.25}$Ge,[21] and MnSi,[22] have been studied. However, these Mn-based compounds usually possess a large MCE accompanied with a FOMT, thus with large thermal and magnetic hysteresis. In the present work, we report reversible room-temperature MCE in Mn$_5$PB$_2$ compound, which is closely related with a SOMT from ferromagnetic (FM) to paramagnetic (PM) state. The maximum values of magnetic entropy change $-\Delta S_M$ are 4.93 and 2.64 J kg^{-1} K^{-1} at 302 K for magnetic field changes of 5 and 2 T, respectively.

Polycrystalline Mn$_5$PB$_2$ was prepared by a multistep power-sintering process. First, Mn, B and red phosorus powers with purity of 99.99% were mixed in desired proportion and pressed into a pellet. The pellet was placed in an Al$_2$O$_3$ crucible sealed in an evacuated quartz tube. The sample was heated at 200 °C for two days and then at 950 °C for seven days. After being cooled down to room-temperature, the sample was pulverized, mixed, and pressed into a pellet again and heated at 950 °C for another seven days and then quenched in water. X-ray diffraction showed that the main phase in the sample is Mn$_5$PB$_2$ compound with tetragonal structure (space group I4/mcm), with a secondary phase Mn$_2$P. The lattice parameters of Mn$_5$PB$_2$ compound are a=b=5.54 Å and c=10.49 Å, which are the same as the previous results.[23] The magnetic properties were measured by using a superconducting quantum inference device magnetometer (Quantum Design, USA) at applied magnetic fields of up to 5 T at temperatures from 280 to 330 K.

The temperature dependence of the magnetization of the Mn$_5$PB$_2$ compound was measured under zero-field cooling (ZFC) and field cooling (FC) processes in a field of 0.01 T as shown in Fig. 1. The Curie temperature T_C was defined as the temperature corresponding to a minimum in the temperature dependence of the first-order derivative of the magnetization (dM/dT) (see the inset of Fig. 1). It can be clearly seen that with increasing temperature, the magnetization drops abruptly at its Curie temperature T_C (=302 K). The reversible behavior above 298 K in ZFC and FC curves (recorded during heating and cooling processes, respectively) indicates that the Mn$_5$PB$_2$ compound undergoes a second-order FM to PM phase transition at 302 K. The secondary
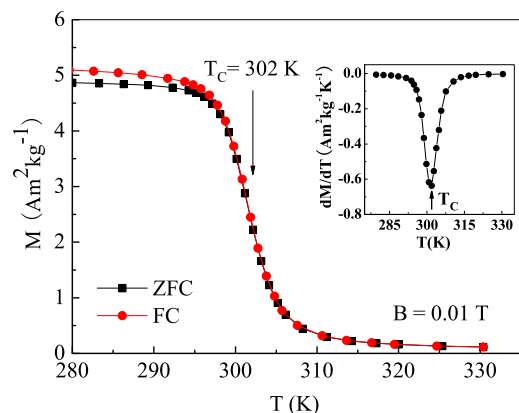

FIG. 1. (Color online) Temperature dependence of the magnetization of Mn$_5$PB$_2$ at 0.01 T. The inset shows the temperature dependence of the first-order derivative of the magnetization (dM/dT).
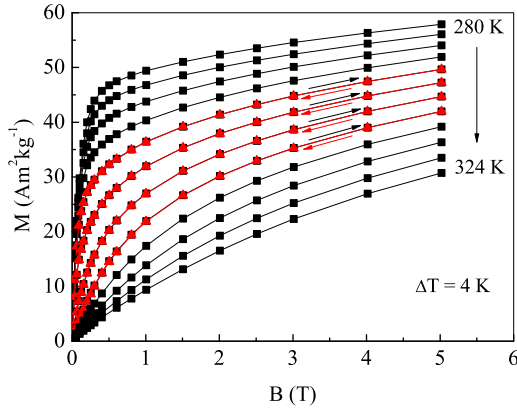
a)Electronic mail: zgxie@imr.ac.cn.

FIG. 2. (Color online) Magnetic isotherms of Mn_5PB_2 in the temperature range of 280–324 K with temperature step of 4 K, measured with increasing-field (solid squares) and decreasing-field (solid triangles) processes. Double arrows indicate the reversible character of isothermal magnetization curves.

phase Mn_2P is antiferromagnetic below its Néel temperature of 103 K,[24] so it has no contribution to magnetic properties of the sample above 103 K, but as a nonmagnetic impurity it will slightly lower the saturation magnetization.

To explore the MCE of the Mn_5PB_2 compound, the isothermal magnetization curves $(M-H)$ in the vicinity of Curie temperature are measured with a maximal field of 5 T and shown in Fig. 2. The solid squares denote the field-increasing process, while the solid triangles correspond to the decreasing-field process. The magnetization increases rapidly at low fields and shows a tendency to saturate with an increase of magnetic field (but not saturated even at 5 T), which is typical for FM materials below its Curie temperature. The magnetization at 280 K is 57.89 A m^2 kg^{-1} at 5 T, which is comparable to the saturation magnetization of pure Ni. Moreover, no magnetic hysteresis between the increasing- and decreasing-field curves is found around the transition temperature, indicating that the FM-PM transition at T_C is of second-order.

Arrott plots (M^2 versus B/M) at different temperatures are shown in Fig. 3, in order to further confirm the type of the phase transition. It is known that the negative slopes (S-shaped curves) in the Arrott plots indicate a first-order phase transition; otherwise, it is a second-order one. It is
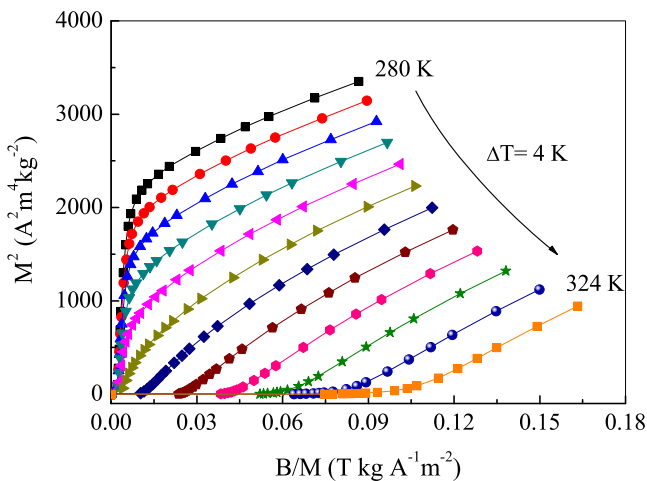

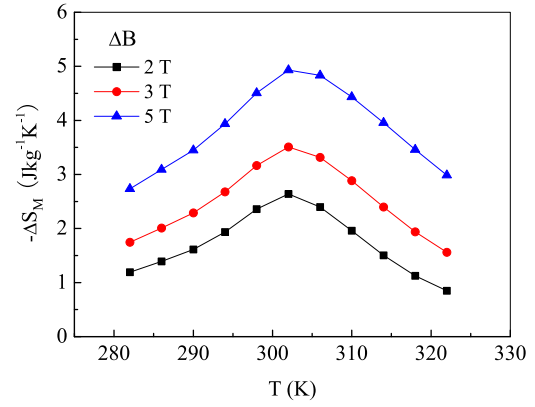FIG. 3. (Color online) Arrott plots of Mn_5PB_2 from 280 to 324 K with the temperature step of 4 K.

FIG. 4. (Color online) Temperature dependences of the magnetic entropy changes $-\Delta S_M$ of Mn_5PB_2 for magnetic field changes ΔB of 2, 3, and 5 T.

clear from the Arrott plots in Fig. 3 that there are no S-shaped curves near T_C, indicating the second-order nature of the FM-PM phase transition, which is consistent with the results obtained above from Figs. 1 and 2.

The magnetic entropy changes $-\Delta S_M$ as a function of temperature and magnetic field for Mn_5PB_2 are calculated from isothermal magnetization curves. By using the Maxwell relation $(\partial S/\partial B)_T = (\partial M/\partial T)_B$, the magnetic entropy changes can be calculated as follows:

$$\Delta S_M(T,B) = S_M(T,B) - S_M(T,0) = \int_0^B \left(\frac{\partial S_M}{\partial B}\right)_T dB$$

$$= \int_0^B \left(\frac{\partial M}{\partial T}\right)_B dB.$$

The temperature dependences of the magnetic entropy changes $-\Delta S_M$ of Mn_5PB_2 for magnetic field changes of 2, 3, and 5 T are presented in Fig. 4. The maximum magnetic entropy changes $-\Delta S_M^{max}$ occur at 302 K, which just corresponds to the FM to PM phase transition. The values of $-\Delta S_M^{max}$ are 2.64, 3.51, and 4.93 J kg^{-1} K^{-1} for magnetic field changes of 2, 3, and 5 T, respectively. The $-\Delta S_M^{max}$ reaches 4.93 J kg^{-1} K^{-1} for a magnetic field change of 5 T, which is comparable to those of other potential Mn-based magnetic refrigerant materials with T_C near room-temperature, such as $MnFe_4Si_3$ (4 J kg^{-1} K^{-1}),[25] $MnFe_{0.15}Co_{0.85}Ge$ (5.3 J kg^{-1} K^{-1}),[26] and $Mn_5Ge_{2.9}Sb_{0.1}$ (6.6 J kg^{-1} K^{-1}).[27] Though the value of $-\Delta S_M^{max}$ at room-temperature of Mn_5PB_2 cannot be compared with the famous Mn-based refrigeration materials, MnFePAs compounds[4] and Ni–Mn-based Heusler alloys,[12–15,19] it should be emphasized that the MCE in the present compound is reversible without any thermal and magnetic hysteresis, associated with a SOMT. It is unsuitable to compare directly the $-\Delta S_M$ value of a material with a SOMT with that of a material with a FOMT. Furthermore, although the secondary phase Mn_2P has no magnetic contribution near room-temperature, as mentioned above, it decreases the value of the saturation magnetization of the sample. If one succeeded in synthesizing the material of single phase Mn_5PB_2, the saturation magnetization and the maximum magnetic entropy change would be enhanced. Moreover, it is expected that the substitution of 3d elements for Mn may increase the maximum magnetic entropy changes, specially, at low magnetic fields.

In conclusion, magnetic properties and MCE of the Mn_5PB_2 compound have been studied. The relatively large reversible MCE with $-\Delta S_M^{max}$ of 4.93 and 2.64 J kg^{-1} K^{-1} are achieved at 302 K for magnetic field changes of 5 and 2 T, respectively. The relatively large magnetic entropy change and the reversible MCE make the Mn_5PB_2 compound (free of rare earths) a promising candidate material for room-temperature magnetic refrigeration application. This work opens a new direction for searching advanced room-temperature magnetic refrigerants, Mn_5PB_2-based MCE materials.

[1] E. Warburg, Ann. Phys. **13**, 141 (1881).

[2] C. B. Zimm, A. Jastrab, A. Sternberg, V. K. Pecharsky, K. A. Gschneidner, Jr., M. Osborne, and I. Anderson, Adv. Cryog. Eng. **43**, 1759 (1998).

[3] J. Glanz, Science **279**, 2045 (1998).

[4] O. Tegus, E. Brück, K. H. J. Buschow, and F. R. de Boer, Nature (London) **415**, 150 (2002).

[5] N. K. Sun, W. B. Cui, D. Li, D. Y. Geng, F. Yang, and Z. D. Zhang, Appl. Phys. Lett. **92**, 072504 (2008).

[6] V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).

[7] V. Provenzano, A. J. Shapiro, and R. D. Shull, Nature (London) **429**, 853 (2004).

[8] H. Wada and Y. Tanabe, Appl. Phys. Lett. **79**, 3302 (2001).

[9] Y. Sun, M. B. Salamon, and S. H. Chun, J. Appl. Phys. **92**, 3235 (2002).

[10] F. X. Hu, B. G. Shen, J. R. Sun, and G. H. Wu, Phys. Rev. B **64**, 132412 (2001).

[11] O. Tegus, B. Fuquan, W. Dagula, L. Zhang, E. Brück, P. Z. Si, F. R. de Boer, and K. H. J. Buschow, J. Alloys Compd. **396**, 6 (2005).

[12] P. A. Bhobe, K. R. Priolkar, and A. K. Nigam, Appl. Phys. Lett. **91**, 242503 (2007).

[13] S. Stadler, M. Khan, J. Mitchell, N. Ali, A. M. Gomes, I. Dubenko, A. Y. Takeuchi, and A. P. Guimarães, Appl. Phys. Lett. **88**, 192511 (2006).

[14] T. Krenke, E. Duman, M. Acet, E. F. Wassermann, X. Moya, L. Mañosa, and A. Planes, Nature Mater. **4**, 450 (2005).

[15] L. Pareti, M. Solzi, F. Albertini, and A. Paoluzi, Eur. Phys. J. B **32**, 303 (2003).

[16] K. A. Gschneidner, Jr., V. K. Pecharsky, and A. O. Tsokol, Rep. Prog. Phys. **68**, 1479 (2005).

[17] B. Li, W. J. Hu, X. G. Liu, F. Yang, W. J. Ren, X. G. Zhao, and Z. D. Zhang, Appl. Phys. Lett. **92**, 242508 (2008).

[18] Q. Zhang, B. Li, X. G. Zhao, and Z. D. Zhang, J. Appl. Phys. **105**, 053902 (2009).

[19] K. Oikawa, W. Ito, Y. Imano, Y. Sutou, R. Kainuma, K. Ishida, S. Okamoto, O. Kitakami, and T. Kanomata, Appl. Phys. Lett. **88**, 122507 (2006).

[20] M. H. Yu, L. H. Lewis, and A. R. Moodenbaugh, J. Appl. Phys. **93**, 10128 (2003).

[21] J. Du, W. B. Cui, Q. Zhang, S. Ma, D. K. Xiong, and Z. D. Zhang, Appl. Phys. Lett. **90**, 042510 (2007).

[22] P. Arora, M. K. Chattopadhyay, and S. B. Roy, Appl. Phys. Lett. **91**, 062508 (2007).

[23] O. Beckman and L. Lundgren, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier, New York, 1991), Vol. 6, Chap. 3.

[24] M. Yessik, Philos. Mag. **17**, 623 (1968).

[25] D. Songlin, O. Tegus, E. Brück, J. C. P. Klaasse, F. R. de Boer, and K. H. J. Buschow, J. Alloys Compd. **334**, 249 (2002).

[26] S. Lin, O. Tegus, E. Brück, W. Dagula, T. J. Gortenmulder, and K. H. J. Buschow, IEEE Trans. Magn. **42**, 3776 (2006).

[27] D. Songlin, O. Tegus, E. Brück, F. R. de Boer, and K. H. J. Buschow, J. Alloys Compd. **337**, 269 (2002).