TOPICAL REVIEW — Magnetism, magnetic materials, and interdisciplinary research

Phase transitions and magnetocaloric effects in intermetallic compounds MnFe*X* (*X*=P, As, Si, Ge)*

O. Tegus(特古斯)†, Bao Li-Hong(包黎红), and Song Lin(松 林)

Inner Mongolia Key Laboratory for Physics and Chemistry of Functional Materials, Inner Mongolia Normal University, Hohhot 010022, *China*

(Received 31 January 2013)

Since the discovery of giant magnetocaloric effect in $MnFeP_{1-x}As_x$ compounds, much valuable work has been performed to develop and improve Fe_2P-type transition-metal-based magnetic refrigerants. In this article, the recent progress of our studies on fundamental aspects of theoretical considerations and experimental techniques, effects of atomic substitution on the magnetism and magnetocalorics of Fe_2P-type intermetallic compounds MnFe*X* (*X*=P, As, Ge, Si) is reviewed. Substituting Si (or Ge) for As leads to an As-free new magnetic material $MnFeP_{1-x}Si(Ge)_x$. These new materials show large magnetocaloric effects resembling MnFe(P, As) near room temperature. Some new physical phenomena, such as huge thermal hysteresis and 'virgin' effect, were found in new materials. On the basis of Landau theory, a theoretical model was developed for studying the mechanism of phase transition in these materials. Our studies reveal that MnFe(P, Si) compound is a very promising material for room-temperature magnetic refrigeration and thermo-magnetic power generation.

Keywords: Fe_2P-type magnetic materials, magnetocaloric refrigeration, thermo-magnetic power generation

PACS: 75.30.Sg, 75.50.Gg **DOI:** 10.1088/1674-1056/22/3/037506

1. Introduction

Magnetic refrigeration as an emerging green technology challenges conventional refrigeration. Recently, research on magnetic refrigeration at room temperature has achieved much, both in developing new magnetic refrigerant materials and new prototype machines.[1–7] Magnetic refrigeration relies upon the magnetocaloric effect (MCE) in some magnetic materials. Therefore, materials with giant MCE are essential for developing room-temperature magnetic refrigeration.

Generally, the heavy rare-earth elements and their compounds with high magnetic moments are considered to be the best candidate materials for providing large MCE near room temperature. Gadolinium and its alloys are the best readily available materials for magnetic refrigeration near room temperature. Gadolinium metal[8,9] undergoes a second-order magnetic phase transition which does not involve magnetic and/or thermal hysteresis, but its alloys $Gd_5(Ge_{1-x}Si_x)_4$[10] undergo a combined first-order structural and magnetic phase transition, which leads to a giant magnetic-field-induced entropy change in the vicinity of their ordering temperatures.

The discovery of the giant MCE in $Gd_5Si_2Ge_2$[2] compounds has triggered vast interest in magnetic cooling near room temperature. In 1998, the first near-room-temperature magnetic refrigerator was demonstrated by Zimm at American Astronautics Technology Center.[11] These two events attracted interest from both scientists and companies who started developing new kinds of room-temperature materials and magnetic-refrigerator designs. Since then, the research on magnetic refrigerant materials with first-order phase transition has been strongly intensified worldwide. Hu *et al*. discovered the giant MCEs in the $NaZn_{13}$-type $La(Fe_{1-x}Si_x)_{13}$ compounds and systematically studied the effects of rare-earth doping, interstitial atoms, and high pressure on the MCE of the compounds.[12–17] Gao *et al*. found that the $La_{1-x}Ca_xMnO_3$ ($x = 0.2$) compound exhibits a large magnetic entropy change near room temperature in a low field change.[7] On the other hand, the large MCE was also found in some transition-metal-based compound systems. Wada *et al*. found the large magnetic entropy change of $MnAs_{1-x}Sb_x$ compounds and reduced its thermal hysteresis by Sb doping.[18,19] Tegus *et al*. discovered the giant MCEs in $MnFeP_{1-x}As_x$ compounds with first-order phase transition, and found that the Curie temperature of the compounds is tunable around room temperature by changing P/As ratio.[3] The spontaneous magnetization of $MnFeP_{1-x}As_x$ compounds is about $4\mu_B$ per chemical formula at 5 K.[20–23]

After the discovery of the giant MCE in $MnFeP_{0.45}As_{0.55}$, the toxic element As was successfully removed from this and similar compounds by substituting Si and Ge for As. Though the new compound MnFe(P, Ge) or MnFe(P, Si) exhibits large MCE, some unexpected and anomalous effects were found. First, there exists a much lower ordering temperature, namely 'virgin' effect, when cooling the sample for the first time from its high-temperature paramagnetic (PM) state to a low-temperature ferromagnetic (FM) state. Neutron diffraction study showed that this effect is most likely to be related to strain effect in the samples.[24] Fortunately, it has been shown

*Project supported by the National Natural Science Foundation of China (Grant Nos. 50661004 and 51161017).

†Corresponding author. E-mail: tegusph@imnu.edu.cn

© 2013 Chinese Physical Society and IOP Publishing Ltd

that this 'virgin' effect has no influence on the MCE performance in the MnFe(P, Si, Ge) compounds upon further temperature cycling. The second phenomenon is an anomalously large thermal hysteresis of the magnetization between the warming and cooling cycles. Although the mechanism of this large thermal hysteresis is not yet completely clear, some ways for reducing the thermal hysteresis have been found by changing the compositions and by using a proper heat-treatment process. A further important issue is how to correctly determine the magnetic entropy change when this quantity is derived from isothermal magnetization measurements at different temperatures. Substantial problems are involved when determining magnetic entropy changes from the mentioned magnetic measurements in conjunction with the Maxwell relation, but a unified procedure is still lacking. In particular, the assessment of MCE in the compounds with large thermal hysteresis presents problems. Recently, a new method has been developed for obtaining reliable values of the magnetic entropy change, in which these problems are circumvented.[25] In this paper, review of the studies on the phase transition and magnetocaloric effects in the Fe_2P-type intermetallic compounds MnFeX (X = P, As, Si, Ge) is presented.

2. Sample preparation

In previous work,[26–28] phosphite–arsenide MnFeX (X=As, P) compounds were prepared by a several-step solid-state reaction method. In our work, the MnFeX (X=P, As, Si, Ge) compounds were synthesized by a mechanically activated solid-diffusion method. The starting materials, Mn chips or powder, Fe powder, Si and Ge chips, red P or Fe_2P (purity 99.5%), As pieces or $FeAs_2$ compounds, were ball milled under vacuum (about 10^{-7} mbar) in a vibrating-ball mill or in a planetary ball mill with a protection gas. During the milling process, solid-state reactions are initiated through repeated deformation and fracture of the powder particles. In order to obtain homogeneous samples, 5–100 grams of the starting materials were ball milled for up to 200 h. After milling, the powder was pressed into pellets and sealed in quartz ampoules in Ar atmosphere of 100–200 mbar. Then, the ampoules were heated at 1100 °C for 2–40 h, followed by annealing at 550–850 °C for 20–50 h. Finally, they were slowly cooled down to ambient temperature. In the whole process, the heating and cooling rate is 180 °C per hour.

3. Assessment of magnetic-entropy change in MnFe(P, As, Ge, Si) compounds

For the determination of entropy change associated with MCEs derived from magnetic measurements, a proper procedure appears to be essential. This is true, especially for materials where the magnetic phase transition is of first order and hence is accompanied by thermal hysteresis. As an example, we have presented the results for some of the $MnFeSi_{0.25}P_{0.75-x}Ge_x$ compounds where the magnetic transition goes hand in hand with a substantial lattice distortion and the first-order phase transition involves a particularly large thermal hysteresis, which is in this case higher than 20 K. $MnFeSi_{0.25}P_{0.75-x}Ge_x$ compounds with nominal compositions $x = 0.08$, 0.10, and 0.12 were prepared by the method described in Section 2. The temperature and magnetic-field dependence of the magnetization were measured in the temperature range from 100 to 375 K and in magnetic field up to 5 T using an SQUID magnetometer (MPMS5).

The temperature dependence of the magnetization measured with increasing temperature at 50 mT is shown in Fig. 1. The transition temperatures, T_h, up to which the FM phase remains metastable, are found to be 275, 293, and 323 K for the compounds with $x = 0.08$, 0.10, and 0.12, respectively. This transition temperature increases with increasing Ge content. The inset in Fig. 1 shows the thermal hysteresis behavior of one of these compounds, $MnFeSi_{0.25}P_{0.64}Ge_{0.1}$, in more detail. Upon cooling for the first time from 293 K (curve 1), a transition occurs at temperature of about 100 K lower than T_h. This behavior (which is called the 'virgin' effect[24]) is irreversible. In the next (curve 3) and all subsequent cooling curves measured during thermal cycling, this effect has disappeared and the transition invariably occurs at $T_c = 269$ K. This temperature is somewhat lower than the transition temperature found in heating curves (293 K, curve 2). The width of the thermal hysteresis between warming and cooling cycles, being a signature of the first-order character of the transition, is about 24 K for this compound. In fact, this means that the high-temperature PM phase remains metastable down to $T_c = 269$ K.

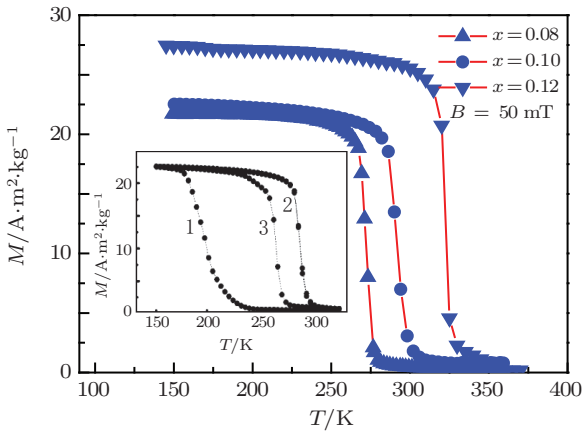


Fig. 1. Temperature dependence of the magnetization of $MnFeSi_{0.25}P_{0.75-x}Ge_x$ compounds measured in a field of 50 mT with increasing temperature. The inset shows the thermal hysteresis behavior of $MnFeSi_{0.25}P_{0.64}Ge_{0.1}$. The sweep rate used for the measurements is 2 K/min.

The magnetic entropy change has been derived from a set of isothermal magnetization data using the Maxwell relation.

The isothermal magnetization curves were measured at different temperatures, increasing with a step of 1 K. This method (here called Method 1) is frequently used to derive the concomitant magnetic-entropy change. The results are shown in Fig. 2(a). It can be seen that due to the first-order phase transition, a large MCE occurs in a very narrow temperature interval. The maximal entropy change for $x = 0.08$ reaches 39 and 110 J/(kgK) in fields changing from 0 to 2 T and 5 T, respectively. According to a new method developed by Caron *et al.*,[25] the isothermal magnetic-entropy change obtained by means of Method 1 does not represent a correct determination of the MCE. A correct assessment would require a special measurement procedure (called Method 2). Specifically, before performing each of the individual isothermal magnetization measurements, the sample has to be warmed up to a temperature located well within the PM regime. Then, the sample has to be carefully cooled in zero field back to the starting temperature of the subsequent isothermal curve. In this way, the uncertainty in the initial state of the sample resulting from the hysteresis can be eliminated. The results obtained by using Method 2 are shown in Fig. 2(b). The values of the magnetic-entropy changes observed with this method are much smaller (but still large) than those obtained by means of Method 1. For example, the maximum magnetic-entropy changes of the compound with $x = 0.08$ are 110 J/(kgK) (by Method 1) and 35.8 J/(kgK) (by Method 2) for a field change from 0 to 5 T. There have been some arguments about the origin of this large discrepancy. Actually, the overestimated values obtained by Method 1 are an artifact due to the application of the Maxwell relation to path-dependent isothermal magnetization data.

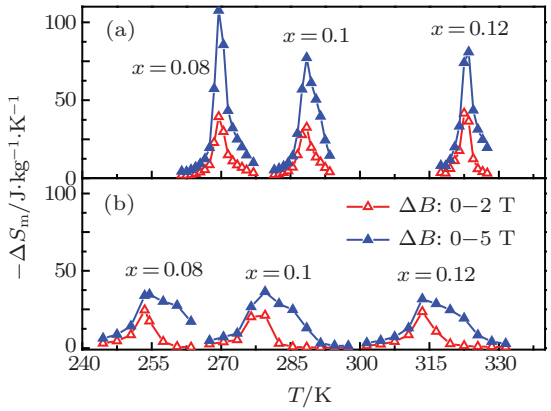


Fig. 2. Isothermal magnetic-entropy change of $MnFeSi_{0.25}P_{0.75-x}Ge_x$ compounds obtained by (a) Method 1 and (b) Method 2.

A comparison between the results obtained by two different experimental methods has been made, and we have demonstrated that the values of the corresponding maximum entropy changes can show extreme differences, i.e., differing by a factor of 3 or even more. Here, we should emphasize that the selection of a correct procedure when measuring the isothermal magnetization curves is essential for the correct assessment of MCE in first-order phase transition materials. These results may be helpful for understanding conflicting results for maximum entropy values reported in the literature, and may also be helpful for searching novel materials showing large MCEs.

4. Hysteretic behaviors of MnFeX (X=P, Si, Ge) compounds

4.1. Theoretical considerations

Landau theory is a simple and successful theory for describing phase transitions. In the framework of this theory, the Gibbs free energy of a magnetoelastic coupling system in the presence of external pressure and magnetic field $H = 0$ is written as

$$g = g_0 + A\sigma^2 + B\sigma^4 + C\sigma^6 + D\omega\sigma^2 + p\omega + \frac{1}{2K}\omega^2, \quad (1)$$

where σ, ω, K, and p represent the spontaneous magnetization, relative volume change, compressibility, and applied pressure, respectively. The parameters A, B, and C are the Landau coefficients, and D represents the coefficient of the third-order coupling between the strain and magnetization. In equilibrium state ($\partial g/\partial\omega = 0$ and $\partial g/\partial\sigma = 0$), we obtain

$$\omega = -K(D\sigma^2 + p), \quad (2)$$

$$\sigma^2 = \frac{-B'^{+}(B'^2 - 12A'C)^{1/2}}{6C}, \quad (3)$$

where $A' = A - DKp$, and $B' = 2B - D^2K$. Equation (2) shows that the relative volume change depends not only on applied pressure p, but also on magnetization, indicating the existence of magnetoelastic effect in the system. This result is same as that in the Bean–Rodbell model.[29]

According to this model, the first-order phase transition is characterized by a set of temperatures, which limit the metastable phase regime as follows: T_0 is the Curie–Weiss temperature at which the theoretical magnetic susceptibility becomes infinite; T_c is the lowest temperature for which the paramagnetic phase can exist; and T_h is the highest temperature for which the ferromagnetic phase can exist. The high-temperature PM phase remains metastable until $A' = 0$. If $A = A_0\,(T - T_0)$, then

$$T_c = T_0 + \frac{DK}{A_0}p. \quad (4)$$

This formula indicates that T_c depends linearly on pressure if only the third-order coupling between the strain and magnetization exists ($D \neq 0$). The low-temperature FM phase remains metastable until $B'^2 = 12A'C$, and T_h is determined by

$$T_h = T_c + \frac{(2B - D^2K)^2}{12A_0C}. \quad (5)$$

Then, the value of thermal hysteresis is given by

$$\Delta T = T_h - T_c = \Delta T_1 + \Delta T_2, \quad (6)$$

where $\Delta T_1 = B^2/(4A_0C)$, and $\Delta T_2 = D^4K^2/(12A_0C) - BD^2K/(2A_0C)$. It is clear that the thermal hysteresis consists of two parts: (i) ΔT_1 is contributed from the competing effect of the magnetizations with different power in the conventional Landau theory; (ii) ΔT_2 is an additional contribution from the coupling of strain and magnetization. If $D = 0$, then $\Delta T_2 = 0$. This implies that the coupling between the magnetization and strain may play an important role, resulting in large thermal hysteresis of $MnFeP_{1-x}T_x$ (T = As, Ge, Si) compounds.

4.2. Experimental results and discussion

The $MnFeP_{1-x}T_x$ (T = As, Ge, Si) compounds were prepared by ball milling and solid-state reaction method, as described in Section 2. $Gd_5Si_{1.7}Ge_{2.3}$ is a single crystal grown by using a floating-zone technique in an NEC image furnace.[22] The $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}$ sample was prepared by an arc melting method followed by a proper heat treatment. The magnetization measurements were carried out in a quantum design SQUID magnetometer.

Figure 3 shows the temperature dependence of the magnetization of six selected compounds. It can be seen that there are mainly three phase-transition temperatures, T_v, T_h, and T_c in $MnFeP_{1-x}T_x$ (T = As, Ge, Si) compounds. The T_v is the transition temperature at which the 'virgin' effect occurs, T_h is the transition temperature observed in the increasing temperature cycle, and T_c is the transition temperature in the second (or further) cooling cycle. The transition temperatures, T_v, T_h, T_c, and the thermal hysteresis, ΔT, of the selected compounds are listed in Table 1. It can be seen that the 'virgin' effect occurs only in the Mn-based compounds, while no 'virgin' effects are observed in the $Gd_5Si_{1.7}Ge_{2.3}$ compound or in $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}$ compound. Furthermore, our recent

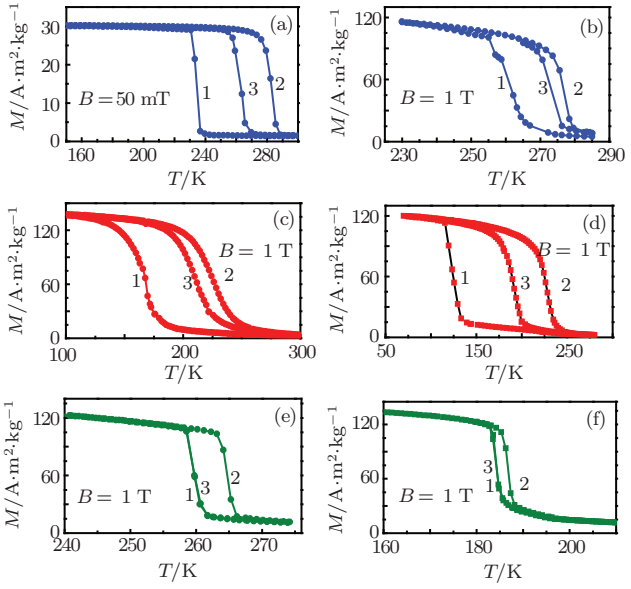


Fig. 3. Temperature dependence of the magnetization of the selected compounds. (a) $MnFeP_{0.5}As_{0.2}Si_{0.3}$; (b) $Mn_{1.1}Fe_{0.9}P_{0.52}As_{0.48}$; (c) $Mn_{1.1}Fe_{0.9}P_{0.84}Ge_{0.16}$; (d) $MnFeP_{0.56}Si_{0.44}$; (e) $Gd_5Si_{1.7}Ge_{2.3}$; (f) $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}$.

Table 1. The transition temperatures, T_v, T_h, T_c, and the thermal hysteresis ΔT of the selected compounds.

Compound	T_v/K	T_c/K	T_h/K	$(\Delta T = T_h - T_c)$/K
$MnFeP_{0.5}As_{0.2}Si_{0.3}$	233	263	283	20
$Mn_{1.1}Fe_{0.9}P_{0.52}As_{0.4}$	262	273	277	4
$Mn_{1.1}Fe_{0.9}P_{0.84}Ge_{0.1}$	168	212	226	14
$MnFeP_{0.56}Si_{0.44}$	123	188	225	37
$Gd_5Si_{1.7}Ge_{2.3}$	–	260	265	5.0
$La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}$	–	184	186.5	2.5

studies showed that the 'virgin' effect occurs not only in Fe_2P-type compounds, but also in other Mn-based compounds, such as MnAs and MnCoGeB compounds.

This 'virgin' effect is a new phenomenon. According to a neutron diffraction study of the $MnFeP_{0.6}Si_{0.4}$ compound,[24,30] the 'virgin' effect is somehow derived from the intrinsic strain effect in the samples. It is necessary to further study the 'virgin' effect. However, one should realize that whether a 'virgin' effect exists in the samples investigated or not, especially in the Mn-based compounds, is still not clear. Otherwise, it may lead to some confusing results. Therefore, we suggest that if you work on Mn-based compounds, it is better first to be sure that whether the samples investigated contain 'virgin' effect or not.

Thermal hysteresis is an intrinsic property of first-order phase transition. As shown in Figs. 3(a)–3(f), all these materials mentioned above involve a certain size of thermal hysteresis. For example, there exists a thermal hysteresis of 37 K in $MnFeP_{0.56}Si_{0.44}$ compound.[31] This is much larger than the MCE in this compound. Figure 4 shows the hysteretic behavior of the $Mn_{1.1}Fe_{0.9}P_{0.82}Ge_{0.18}$ compound in a field of 5 T, in several heating and cooling cycles, which are labeled with numbers 1–4. The maximum thermal hysteresis is observed for a full cycle from FM state to PM state, and then from PM state to FM state. In the other cycles 1–3, the magnetization curves at cooling process are different, and depend on the history of the cycles. This result shows that the magnetic behavior is strongly dependent on the history of the cycles. Therefore, a question arises, whether the first-order phase transition materials can be used in a real magnetic refrigeration cycle or not. The solution to the question lies in whether it is possible

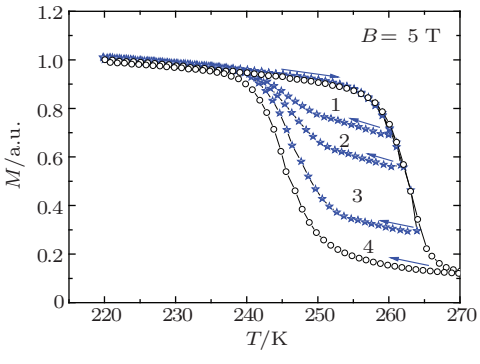


Fig. 4. Temperature dependence of the magnetization of $Mn_{1.1}Fe_{0.9}P_{0.82}Ge_{0.18}$ compound measured in a field of 5 T for several warming and cooling cycles.

to tune the thermal hysteresis as small as possible. In the case of $Gd_5(Si,Ge)_4$ compound, addition of a small amount of Fe can significantly reduce the thermal hysteresis or even eliminate it without losing the large MCE.[32] In the case of La(Fe, $Si)_{13}$ compound, replacement of Fe by Co and an addition of C can also reduce the thermal hysteresis.[33,34] In recent years, we have studied the relationship between the thermal hysteresis and the compositions, applied field and applied pressure in MnFe(P, As, Si) compounds. Our results show that the thermal hysteresis can be tuned by changing compositions, in some cases even by making the thermal hysteresis less than 1 K.

A field-induced first-order transition is important to produce large magnetic entropy change. The existence of field hysteresis, over a range of temperature above the Curie temperature (T_c), provides clear evidence of the first-order nature of the PM–FM phase transition in the compounds mentioned above. Figure 5(a) displays the magnetization of the $MnFeP_{0.5}As_{0.5}$ compound measured at 301 K ($T_c = 282$ K). It can be seen that there is no field-induced transition until a maximum field of 1 T. Therefore, the lines of increasing field and decreasing field linearly overlap with each other, indicating that the sample is in the PM state. In a field of 2 T, we observe a field-induced phase transition from the PM state to the FM state, and a field hysteresis of about 0.16 T between the increasing field and decreasing field curves. For higher applied field up to 5 T, the field-induced transitions overlap with each other, and there are no differences in field hysteresis with 2-T field curves. It is important to notice that the transition starts at a field of 1.5 T and completes at 2 T. This means that if one expects to obtain a large MCE in this compound at 301 K, a field larger than 1.5 T is needed. As shown in Fig. 5(b), substituting Si for As makes the field hysteresis pronouncedly large. In this case, for example, at 270 K we can see a field-induced transition starting from 3 T, but it is not completed until 5 T. In the decreasing field process, the compound remains in the FM state, and the field change does not lead to atomic level spin disorder. Therefore, the increasing field and decreasing field process is a magnetically irreversible process. In the increasing field process, a large MCE is produced by field-induced transition. However, in the decreasing field process, we could not observe the same large effect. Now, most prototype machines operate with a maximum field of 1.5 T, which is a realistic situation for applications, and can be reached by permanent magnet arrangements. This suggests that the materials with small field hysteresis and small critical field (< 1.5 T) are needed for practical applications.

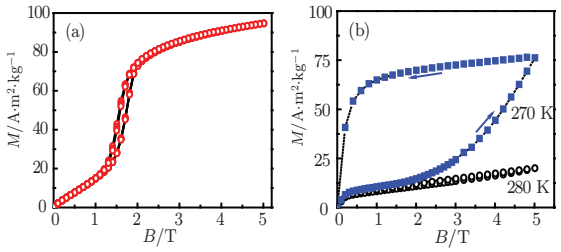


Fig. 5. (a) Field-induced phase transition and field hysteresis of $MnFeP_{0.5}As_{0.5}$ compound measured at 310 K. (b) Magnetization loops of $MnFeP_{0.5}As_{0.2}Si_{0.3}$ compound measured at 270 and 280 K, respectively.

The results in this section lead to the following conclusions.

1) An abnormal phase transition behavior, the 'virgin' effect, is found in some Mn-based compounds. The origin of the effect is not clearly understood yet. It is worth checking whether a 'virgin' effect exists in any investigated compounds, in order to avoid some confusing results.

2) The thermal hysteresis exists in all first-order phase transition materials. The large size of the thermal hysteresis and the heat-cycle history dependence of magnetization make these materials unsuitable for magnetic cooling applications. However, the thermal hysteresis can be tuned by changing compositions. If we select a proper substitution element, the thermal hysteresis can be reduced to less than 1 K. The first-order phase transition materials could be used as refrigerants at the expense of heat loss.

3) Field-induced phase transition is important for getting large MCE. For a first-order phase transition material, at a given temperature T, if there is a reversible field-induced transition, then there is a reversible MCE. For the magnetic field generated by permanent magnets (maximum field of 1.5 T), the materials with small field hysteresis and small critical field (< 1.5 T) are needed.

4) Analysis based on Landau theory shows that the coupling between the magnetization and strain plays an important role in the phase transition of these materials, and contributes an additional part to the thermal hysteresis.

5. Atomic substitution effects on magnetic and magnetocaloric properties of MnFe(P, Si) compounds

From the raw-material cost and production point of view, the MnFe(P, Ge) compounds appear to be unattractive for practical applications, because of high price of Ge. Therefore, the replacement of As by Si in MnFe(P, As) compounds becomes one of the most prominent studies in moving toward making high-performance room-temperature magnetic refrigerants. Some efforts have been made to reduce thermal hysteresis and to optimize performance by tuning compositions. In this section, we report on the effects of Mn/Fe ratio change,

P/Si ratio change, and Co substitutions on the MCE in this compound system.

5.1. $Mn_{1.3}Fe_{0.7}P_{1-x}Si_x$ compounds

Figure 6 shows temperature dependence of the magnetization of $Mn_{1.3}Fe_{0.7}P_{1-x}Si_x$ measured in an applied field of 0.05 T with increasing temperature and subsequently with decreasing temperature. Clearly, the Curie temperature decreases with decreasing Si content, showing that the P/Si ratio change plays an important role in tuning the Curie temperature. The thermal hysteresis (ΔT_{hys}) derived from these data is displayed in Table 2. It can be seen that ΔT_{hys} increases with increasing phosphorus content. The value of ΔT_{hys} is 10.4 K for $x = 0.45$. The sharp change in magnetization and the large thermal ΔT_{hys} indicate that the transition is of the first order.

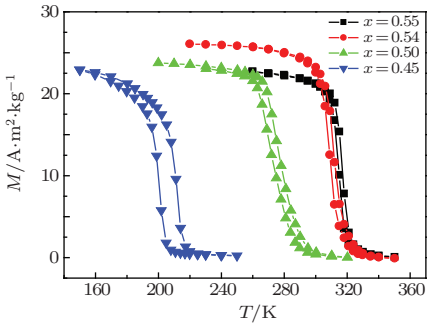


Fig. 6. Temperature dependence of the magnetization of $Mn_{1.3}Fe_{0.7}P_{1-x}Si_x$, measured in a field of 0.05 T in warming and cooling processes.

Table 2. Curie temperature, maximal magnetic entropy change, and thermal hysteresis of $Mn_{1.3}Fe_{0.7}P_{1-x}Si_x$ compounds.

x	T_c/K	$-\Delta S_{max}$/J·kg^{-1}·K^{-1}	ΔT_{hys}/K
0.55	320	9.3	2.3
0.54	312	8.0	2.6
0.50	272	6.4	5.0
0.45	209	11.3	10.4

The magnetic entropy change, $-\Delta S_m(T, \Delta B)$, was numerically derived from the isothermal magnetizations based on the Maxwell relation. The results are shown in Fig. 7. For an external-field change from 0 to 1.5 T, the maximum value of the entropy change is about 11.3 J/(kgK) for $x = 0.45$.

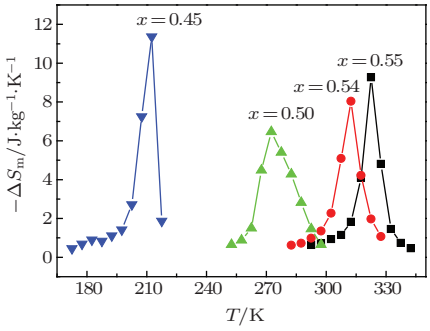


Fig. 7. Temperature dependence of the magnetic entropy change in $Mn_{1.3}Fe_{0.7}P_{1-x}Si_x$ compounds at $B = 1.5$ T with $x = 0.55$, 0.54, 0.50, and 0.45.

In conclusion, the variation of P/Si ratio offers a possibility of tuning the Curie temperature and thermal hysteresis in $Mn_{1.3}Fe_{0.7}P_xSi_{1-x}$ compounds.

5.2. $Mn_{1.3}Fe_{0.7-\delta}P_{0.45}Si_{0.55}$ compounds

Dung *et al.*[35] reported that a small reduction of Fe contents is useful to gain good performance of $MnFeP_{0.5}Si_{0.5}$ compounds. In order to more specifically study the optimal compositions and properties, we studied the effects of a slight change of Fe contents on the magnetic properties of the $Mn_{1.3}Fe_{0.7}P_{0.45}Si_{0.55}$ compound.

Figure 8 shows the scanning electron microscopy (SEM) image of the $Mn_{1.3}Fe_{0.7}P_{0.45}Si_{0.55}$ compound. It can be seen that the compound mainly consists of one single phase (gray areas) and some holes (black areas) about 5%.

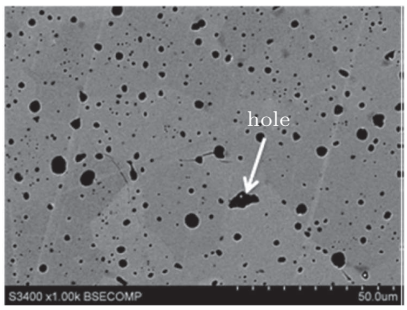


Fig. 8. SEM image of $Mn_{1.3}Fe_{0.7}P_{0.45}Si_{0.55}$ compound.

Figure 9 shows the temperature dependence of the magnetization of $Mn_{1.3}Fe_{0.7-\delta}P_{0.45}Si_{0.55}$ compounds, when heating the as-prepared sample and in subsequent cooling process. The Curie temperature and thermal hysteresis of the compounds are listed in Table 3. Note that the thermal hysteresis of the compounds can be reduced to 1 K when the Fe content is 0.68 and 0.66.

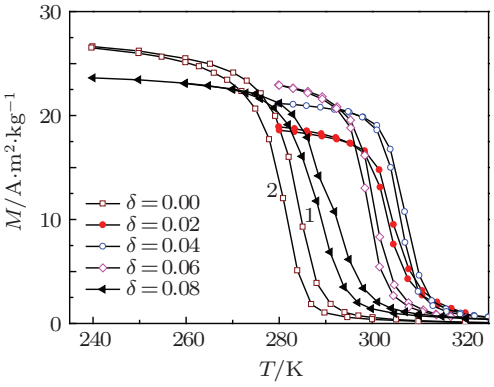


Fig. 9. Temperature dependence of the magnetization of $Mn_{1.3}Fe_{0.7-\delta}P_{0.45}Si_{0.55}$ compounds measured in a field of 0.05 T.

The temperature dependence of magnetic entropy changes in $Mn_{1.3}Fe_{0.7-\delta}P_{0.45}Si_{0.55}$ compounds are shown in Fig. 10. The maximum value of magnetic entropy change is in the range from 7.3 to 7.9 J/(kgK) when δ increases from 0 to 0.06, for a field change from 0 to 1.5 T. These results show

that the Curie temperature of the compounds is very sensitive to Fe content, and a proper reduction of Fe contents is even useful to reduce thermal hysteresis in these compounds.

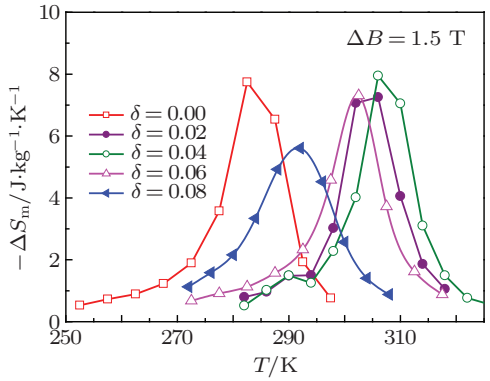


Fig. 10. Isothermal magnetic entropy change of $Mn_{1.3}Fe_{0.7-\delta}P_{0.45}Si_{0.55}$ compounds in a field change from 0 to 1.5 T.

Table 3. Curie temperature, thermal hysteresis, and maximal isothermal magnetic entropy change in $Mn_{1.3}Fe_{0.7-\delta}P_{0.45}Si_{0.55}$ compounds for a field change from 0 to 1.5 T.

δ	T_c/K	ΔT_{hys}/K	$-\Delta S_{max}$/J·kg^{-1}·K^{-1}
0.00	284	3.0	7.7
0.02	305	1.0	7.3
0.04	307	1.0	7.9
0.06	300	1.5	7.3
0.08	290	3.0	5.6

In conclusion, the Curie temperature can be tuned from 284 K ($\delta = 0$) to 307 K ($\delta = 0.04$) by reducing the Fe contents. An optimization of Fe contents is useful to increase T_c and to reduce thermal hysteresis.

5.3. $Mn_{1.3}Fe_{0.7-x}Co_xP_{0.46}Si_{0.54}$ compounds

The temperature dependences of the magnetization curves of the $Mn_{1.3}Fe_{0.7-x}Co_xP_{0.46}Si_{0.54}$ compounds with $x =$ 0, 0.025, 0.05, and 0.1 measured in warming and cooling processes in a field of 0.05 T are shown in Fig. 11. It can be seen that the thermal hysteresis depends on Co content, but the dependence is quite weak.

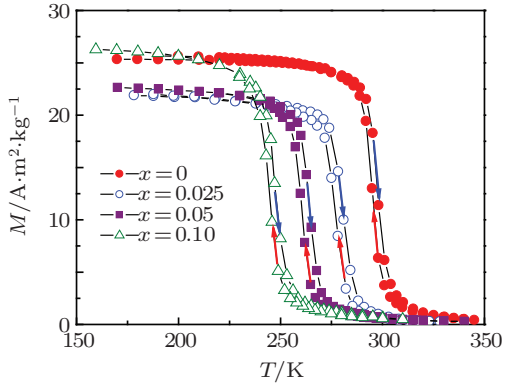


Fig. 11. Temperature dependence of the magnetization of $Mn_{1.3}Fe_{0.7-x}Co_xP_{0.46}Si_{0.54}$ measured in a field of 0.05 T when warming the as-prepared sample and in subsequent cooling process.

Table 4. Thermal hysteresis ΔT_{hys}, maximal isothermal magnetic entropy change $-\Delta S_{max}$ (at $B = 1.5$ T), and adiabatic temperature change ΔT_{ad} (at $B = 1.48$ T) in $Mn_{1.3}Fe_{0.7-x}Co_xP_{0.46}Si_{0.54}$ compounds.

x	ΔT_{hys}/K	$-\Delta S_{max}$/J·kg^{-1}·K^{-1}	ΔT_{ad}/K
0	2.8	8.3	2.2
0.025	3.0	7.6	2.0
0.050	3.0	7.2	2.2
0.10	2.6	5.7	–

Figure 12(a) displays the temperature dependence of $-\Delta S_m$ for the compounds $Mn_{1.3}Fe_{0.7-x}Co_xP_{0.46}Si_{0.54}$ ($x = 0$, 0.025, 0.05, 0.1). The magnetic entropy change decreases a little for Co substitution, compared with the change in the $Mn_{1.3}Fe_{0.7}P_{0.46}Si_{0.54}$ compound, but the width of the ΔS_m peak becomes broad with increasing Co content. Figure 12(b) shows the temperature dependence of adiabatic temperature change of $Mn_{1.3}Fe_{0.7-x}Co_xP_{0.46}Si_{0.54}$ ($x = 0$, 0.025, 0.05) for a field change from 0 to 1.48 T. The direct measurement of adiabatic temperature change was performed at Baotou Institute of Rare Earths. The maximal ΔT_{ad} is about 2.2, 2.0, and 2.2 K for $x = 0$, 0.025, and 0.05, respectively, which is larger than the reported values for the $LaFe_{11}Co_{0.9}Si_{1.1}$ compound.[36] The parameters are listed in Table 4.

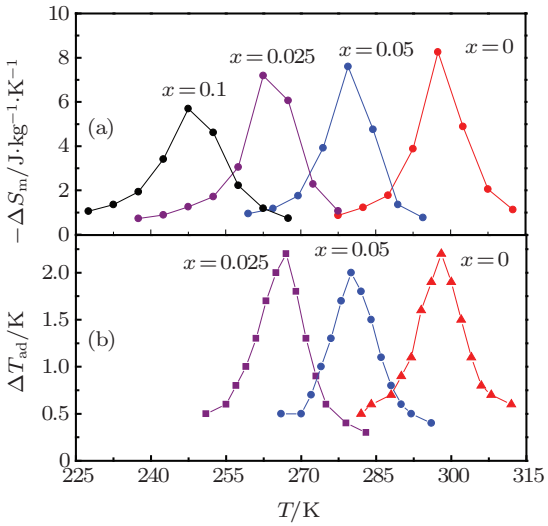


Fig. 12. (a) Isothermal magnetic-entropy changes of compounds $Mn_{1.3}Fe_{0.7-x}Co_xP_{0.46}Si_{0.54}$ ($x = 0$, 0.025, 0.05, 0.1) for a field change from 0 to 1.5 T. (b) Temperature dependence of adiabatic temperature change (ΔT_{ad}) of $Mn_{1.3}Fe_{0.7-x}Co_xP_{0.46}Si_{0.54}$ ($x = 0$, 0.025, 0.05) for a field change from 0 to 1.48 T.

In conclusion, $Mn_{1.3}Fe_{0.7-x}Co_xP_{0.46}Si_{0.54}$ ($x = 0$, 0.025, 0.05, 0.1) compounds show large MCE in the temperature range from 247 to 298 K. A significant reduction of thermal hysteresis and tunable T_c for the compounds have been achieved by tuning the compositions.

5.4. Specific heat studies on MnFe(P, Si) compounds

Specific-heat studies are very important for understanding the heat effects in phase transition. Because of the latent heat of first-order phase transition, it is very difficult to

measure the specific heat of first-order phase transition materials with conventional methods. Here, we report specific-heat measurements of MnFe(P,Si) compounds by using differential scanning calorimetry (DSC), which has the advantages of easy implementation, shorter measurement time, smaller samples, and high accuracy.

Figure 13 shows the specific heat of $Mn_{2-x}Fe_xP_{0.51}Si_{0.49}$ ($x = 0.8, 0.85, 0.9, 0.95, 1.0$) compounds. With the increase in Fe content, the peak at specific heat moves from 280.8 K for $x = 0.8$ to 345.7 K for $x = 1.0$. On the basis of Debye model, analysis of the specific heat of these compounds has been made. The electronic contribution to the specific heat is taken as $C_e = 0.016T$.[37] The lattice contribution to the specific heat C_l is obtained by fitting the experimental data. As shown in Fig. 14, the best fit value of Debye temperature is 450 K for the $Mn_{1.2}Fe_{0.8}P_{0.51}Si_{0.49}$ compound. The magnetic contribution to the specific heat is obtained by using $C_m = C_p - C_l - C_e$. The results are shown in Fig. 15 for the $Mn_{1.2}Fe_{0.8}P_{0.51}Si_{0.49}$ compound. The magnetic entropy change ΔS_m of these compounds have been determined from the $T - S_m$ curves. The phase transition temperature, magnetic entropy change, and latent heat of the $Mn_{2-x}Fe_xP_{0.51}Si_{0.49}$ compounds are listed in Table 5.

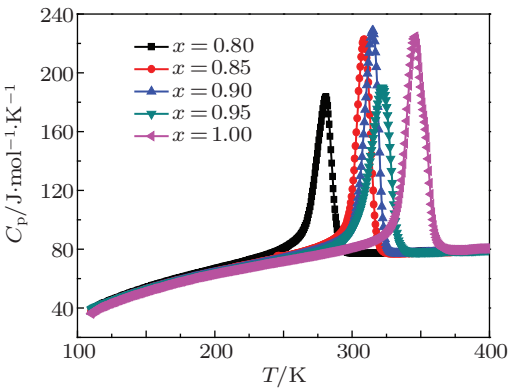


Fig. 13. Temperature dependence of specific heat of $Mn_{2-x}Fe_xP_{0.51}Si_{0.49}$ compounds.

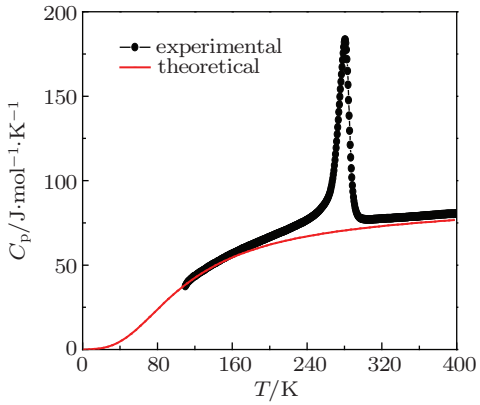


Fig. 14. Temperature dependence of specific heat of $Mn_{1.2}Fe_{0.8}P_{0.51}Si_{0.49}$ compound at the Debye temperature of 450 K.

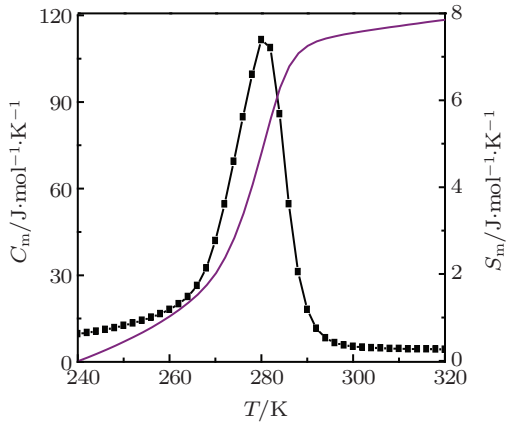


Fig. 15. Temperature dependence of magnetic specific heat and magnetic entropy of $Mn_{1.2}Fe_{0.8}P_{0.51}Si_{0.49}$ compound.

Table 5. Phase transition temperature, entropy change, and latent heat of the $Mn_{2-x}Fe_xP_{0.51}Si_{0.49}$ compounds. Latent heat was derived by using $L = \Delta S_m T_c$.

x	T_c/K	ΔS_m/J·mol^{-1}·K^{-1}	L/kJ·mol^{-1}
0.8	280.8	7.5	2.1
0.85	308.8	8.1	2.5
0.9	315.1	8.4	2.7
0.95	322.0	9.8	3.2
1.0	345.7	1 0	3.5

The DSC study of the heat effects in MnFe(P, Si) compounds with transition temperatures close to room temperature is a more informative and reliable method than magnetization isotherms. This method provides an effective and easily accessible means to obtain MCE data of the first-order transition materials, especially useful for designing a cascade system.

6. Summary and outlook

We have systematically investigated the MCEs and relevant physical properties in the Fe_2P-type MnFe(P, T) (T=As, Ge, Si) compounds. In this paper, the recent developments in sample preparation, structural, magnetic, and magnetocaloric properties, and phase transition in the Fe_2P-type intermetallic compounds MnFeX (X=P, As, Ge, Si) were reviewed.

(1) For the determination of magnetic entropy change in first-order phase transition materials as derived from magnetic measurements, a proper measurement procedure and a correct assessment appear to be essential for searching and investigating new magnetic refrigerants.

(2) The toxic element As has been successfully replaced by either Ge or Si. The new material MnFeX (X=P, Ge) or MnFeX (X=P, Si) shows large MCEs, resembling those observed in MnFeX (X=P, As) near room temperature.

(3) Some new phenomena, such as the 'virgin' effect and huge thermal hysteresis, were found in the MnFeX (X=P, Ge) and MnFeX (X=P, Si) compounds. A theoretical model based on Landau theory is proposed to investigate the origin of the thermal hysteresis and the mechanism of the phase transition.

(4) Considering the raw-material cost and the safety of both production and environment, the MnFe(P,Si) compounds appear to be more attractive for practical applications. An effective tuning of the compositions, such as Mn/Fe ratio change, P/Si ratio change, a proper reduction of Fe contents, and atomic substitution of Fe by Co, could lead to the properties that are needed for applications. In addition, the MnFe(P, Si) compounds show excellent thermomagnetic power generation properties.[38]

Finally, the Fe_2P-type intermetallic compounds MnFeX (X=P, As, Ge, Si) are some of the most attractive room-temperature magnetic refrigerants, and may have applications in thermomagnetic electricity generation.

References

[1] Brown G V 1976 *J. Appl. Phys.* **47** 3673
[2] Pecharsky V K and Gschneidner K A 1997 *Phys. Rev. Lett.* **78** 4494
[3] Tegus O, Brück E, Buschow K H J and de Boer F R 2002 *Nature* **415** 150
[4] Shen B G, Sun J R, Hu F X, Zhang H W and Cheng Z H 2009 *Adv. Mater.* **21** 4545
[5] Fujieda S, Fujita A and Fukamichi K 2002 *Appl. Phys. Lett.* **81** 2002
[6] Yu B F, Liu M, Peter W, Egolf B and Andrej K 2010 *Int. J. Refrigeration* **33** 1029
[7] Guo Z B, Du Y W, Zhu J S, Huang H, Ding W P and Feng D 1997 *Phys. Rev. Lett.* **78** 1142
[8] Dan'kov S Y and Tishin A M 1998 *Phys. Rev. B* **57** 3478
[9] Grzegorz B, Geldart D J W and Mary A W 1993 *Phys. Rev. B* **47** 14247
[10] Pecharsky V K and Gschneidner K A 1997 *Appl. Phys. Lett.* **70** 3299
[11] Zimm C, Jastrab A, Strenberg A, Pecharsky V, Gschneidner K A, Osborne M and Anderson I 1998 *Adv. Cryog. Eng.* **43** 1759
[12] Hu F X, Shen B G, Sun J R, Cheng Z H, Rao G H and Zhang X X 2001 *Appl. Phys. Lett.* **78** 3675
[13] Hu F X, Shen B G and Sun J R 2000 *Appl. Phys. Lett.* **76** 3460
[14] Hu F X, Shen B G, Sun J R and Zhang X X 2000 *Chin. Phys.* **9** 550
[15] Hu F X, Shen B G, Sun J R, Wang G J and Cheng Z H 2002 *Appl. Phys. Lett.* **80** 826
[16] Hu F X, Shen B G, Sun J R and Cheng Z H 2001 *Phys. Rev. B* **64** 012409
[17] Shen B G, Hu F X, Dong Q Y and Sun J R 2013 *Chin. Phys. B* **22** 017502
[18] Wada H and Tanabe Y 2001 *Appl. Phys. Lett.* **79** 3302
[19] Wada H, Asano T, Ilyn M and Tishin A M 2007 *J. Magn. Magn. Mater.* **310** 2811
[20] Tegus O, Brück E, Zhang L, Dagula, Buschow K H J and de Boer F R 2002 *Physica B* **319** 174
[21] Tegus O, Brück E, Dagula, de Boer F R and Buschow K H J 2002 *IEEE Trans. Magn.* **38** 2753
[22] Tegus O 2003 *Novel Materials for Magnetic Refrigeration* (Ph.D. thesis) (Amsterdam: University of Amsterdam)
[23] Brück E, Ilyn M, Tishin A M and Tegus O 2005 *J. Magn. Magn. Mater.* **290** 8
[24] Zhang L 2005 *Unusual Magnetic Behavior of Some Rare-Earth and Manganese Compounds* (Ph.D. thesis) (Amsterdam: University of Amsterdam)
[25] Caron L, Ou Z Q, Nguyen T T, Cam Thanh D T, Tegus O and Brück E 2009 *J. Magn. Magn. Mater.* **321** 3559
[26] Beckman O and Lundgren L 1991 *Handbook of Magnetic Materials* **6** 181
[27] Bacmann M, Soubeyroux J L, Barrett R, Fruchart D, Zach R, Niziol S and Fruchart R 1994 *J. Magn. Magn. Mater.* **134** 59
[28] Zach R, Malaman B, Bacmann M, Fruchart R, Niziol S, Le Caer G, Soubeyroux J L, Zukrowski J and Fruchart D 1995 *J. Magn. Magn. Mater.* **147** 201
[29] Bean C B and Rodbell D S 1962 *Phys. Rev.* **126** 104
[30] Zhang L, Može O, Prokeš K, Tegus O and Brück E 2005 *J. Magn. Magn. Mater.* **290** 679
[31] Thanh D T C, Brück E, Trung N T, Klaasse K C P, Buschow K H J, Ou Z Q, Tegus O and Caron L 2008 *J. Appl. Phys.* **103** 07B318
[32] Provenzano V, Shapiro A J and Shull R D 2004 *Nature* **429** 853
[33] Sun J, Dong QY, Li Y X and Sun J R 2008 *J. Alloy. Compd.* **458** 115
[34] Balli M, Fruchart D and Gignoux D 2008 *Appl. Phys. Lett.* **92** 232505
[35] Dung N H, Zhang L, Ou Z Q and Brück E 2011 *Appl. Phys. Lett.* **99** 092511
[36] Balli M, Fruchart D, Sari O, Gignoux D, Huang J H and Egolf W 2009 *J. Appl. Phys.* **106** 023902
[37] Beckman O, Lundgren L and Svedlindh P 1982 *Phys. Scr.* **25** 679
[38] Bilige, Tegus O, Yiriletu and Shi H R 2012 *Acta Phys. Sin.* **61** 077103 (in Chinese)