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Hydrogenating process and magnetocaloric effect in $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}H_x$ hydrides

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ABSTRACT

Interstitial $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}H_x$ hydrides with large magnetocaloric effect are prepared. It is found that the addition of carbon atoms can lower the rate of hydrogen absorption/release, which is beneficial to an accurate control of hydrogen content. The Curie temperature T_C can be adjusted to the room temperature by changing the carbon/hydrogen content. The introduction of carbon atoms leads to a remarkable reduction of thermal/magnetic hysteresis because the first-order magnetic transition is weakened. The maximal magnetic entropy change of $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}H_{1.2}$ is found to be 22.1 J/kg K at $T_C = 321$ K without hysteresis loss for a field change of 0–5 T.

1. Introduction

Magnetic materials with large magnetocaloric effects (MCEs) have been intensively studied in the past decades because of their potential applications as magnetic refrigerants. Large MCE around the transition temperature has been found in many materials with a first-order phase transition [1–6]. Among these materials, the cubic $NaZn_{13}$-type $LaFe_{13-x}Si_x$ is one of the most attractive compounds because of its large MCE, easy preparation and low cost [6]. Although, the first-order phase transition materials each have usually a large magnetic entropy change (ΔS_M), magnetic hysteresis loss happens inevitably [7], which greatly reduces the actual refrigerant capacity (RC) [8]. Many efforts have been made to increase the MCE, in the meantime reducing or even eliminating the hysteretic loss. The substitution of Co for Fe in $LaFe_{13-x}Si_x$ pushes T_C to room temperature and depresses the hysteresis loss by driving the phase transition from the first-order to the second-order. However, it simultaneously leads to a remarkable decrease of ΔS_M [9]. Partially replacing La with Pr [10] or Nd [11] increases MCE, but hysteresis loss also grows concurrently. The interstitial carbides prepared by arc-melting are chemically stable. However, with the increase of carbon content, the MCE decreases drastically, the α-Fe appears and the $NaZn_{13}$-type phase is difficult to form [12,13]. In contrast, by annealing the sample in a hydrogen environment, hydrogen can be introduced into the interstitial sites of the lattice. This leads to a significant increase in Curie temperature, rising to the room temperature, while ΔS_M remains large and hysteresis loss keeps small [14–18]. However, the magnetic phase transition temperature and hysteresis loss are sensitive to the content of hydrogen in the $LaFe_{13-x}Si_x$-based hydrides. Therefore, an accurate control of hydrogen content is very important in the gas–solid reaction processing. In the present paper, we report on the effect of carbon addition on hydrogenating process and magnetocaloric effect in the $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}H_x$ hydrides.

2. Experimental

Samples with the nominal compositions of $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ and $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}$ were firstly prepared by arc-melting an appropriate quantity of the starting materials (99.9% in purity) in an atmosphere of argon gas. The weights of the arc-melted $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ and $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}$ buttons are about 15.8 and 13.2 g, respectively. The samples were subsequently annealed at 1223 K for two weeks then quenched into liquid nitrogen. Then, the interstitial hydrogen was introduced into the $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}$ compound by gas–solid phase reaction using commercial P–C–T (pressure–composition–temperature) equipment. The hydrogen absorption was carried out by annealing $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}$ at 623 K, in a chamber with different hydrogen pressures. The hydrogen contents in $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}H_x$ were determined by ideal gas law ($PV = nRT$), where P is the hydrogen pressure, V is the volume of the chamber, n is the mole number of H_2 in the chamber, R is the ideal gas constant (8.3145 J/mol K), and T is the temperature at which the compounds were annealed in H_2. The concentration of hydrogen in the compound is determined from the difference in weight between before and after hydrogenation and the hydrogen pressures in the sealed chamber. Powder X-ray diffraction (XRD) measurement of the carbide was performed using Cu K_α radiation to identify phase purity and crystal structure. It is shown that the sample is single-phase compound with cubic $NaZn_{13}$-type structure. Magnetization was

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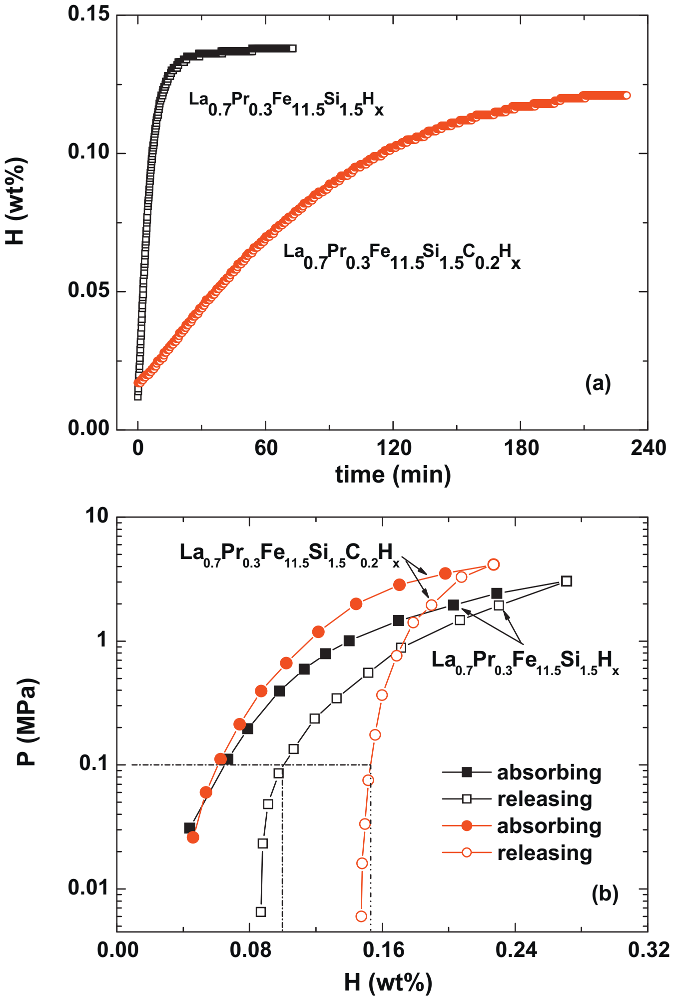

Fig. 1. (a) Variations of absorbing hydrogen with time for $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ and $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}$ under 0.1 MPa (1 atm) hydrogen pressure at 623 K. (b) Hydrogen pressure dependent hydrogen content (wt%) for $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ and $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}$ measured at 623 K in absorbing and releasing processes.

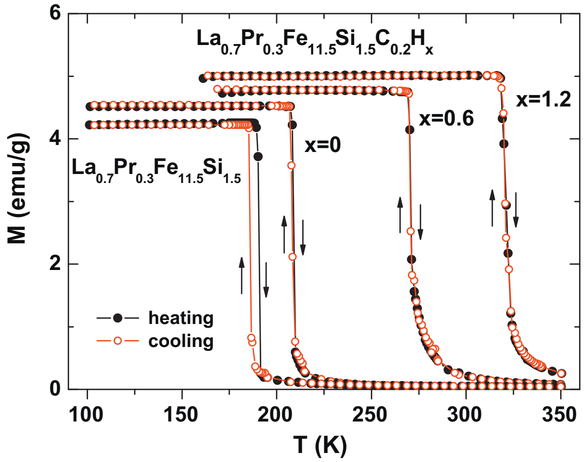

Fig. 2. Temperature dependent magnetizations for $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ and $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}H_x$ ($x = 0$, 0.6 and 1.2) measured under 0.01 T in heating and cooling processes.

measured as a function of temperature and magnetic field, using a superconducting quantum interference device magnetometer.

3. Results and discussion

Fig. 1(a) shows the hydrogen absorbing kinetic curves for the $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ and $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}$ compounds, obtained at a starting hydrogen pressure of 0.12 MPa and a temperature of 623 K. It is found that the absorbing process is completed in about 20 min for $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ while it proceeds up to 3 h for $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}$. The final hydrogen pressures after the absorption for both compounds are less than 1 atm. The phenomena indicate that introducing carbon atoms into $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ lattices can decrease the velocity of hydrogen absorption, which is propitious for an accurate control of hydrogen content. The P–C–T relations for both $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ and $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}$ at 623 K are shown in Fig. 1(b), which provide additional data for the carbon-enhanced hydrogen content stability. For the carbon-free compound, the absorbing curve and the releasing curve are relatively close to each other, and about 0.097 wt% hydrogen (~0.8 H per formula unit) is residual after hydrogen releasing. By contrast, the releasing process is lag behind the absorbing process for $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}$ and about 0.153 wt% (~1.2 H per formula unit) is remnant. This also indicates that the addition of interstitial carbon atom not only slows down hydrogen absorbing but also prevents hydrogen from being released. This means that the $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}H_x$ compounds has better hydrogen content stability than $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}H_x$ under normal atmosphere, which is highly desired in the sense of practical application. It is possible that there are distinctive diffusion paths for the interstitial atoms in the lattice. The pre-occupied interstitial carbon atoms, which occupy the 24d sites [19], distort the local lattice because its atomic radius is larger than hydrogen. This may lead to the blocking of the diffusion paths, depressing rate of the hydrogen absorption/release.

Fig. 2 shows the thermomagnetic *M*–*T* curves of $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ and $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}H_x$ ($x = 0$, 0.6 and 1.2), measured in the heating and the cooling processes in a field of 0.01 T. The Curie temperature T_C is found to increase with the hydrogen content from 189 K for $x = 0$ to 321 K for $x = 1.2$. It shows a temperature hysteresis (~4 K) of the magnetic transitions for $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$. The thermal hysteresis is smaller than 1 K for $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}$ and even invisible for $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}H_x$ with $x = 0.6$ and 1.2. This indicates the weakening of the first-order nature of the magnetic transition through introducing the interstitial carbon and hydrogen. The spin fluctuation at the transition temperature may be modified by the interstitial site C/H, which leads to a lower energy barrier separating the PM from the FM state in the free energy curve by renormalization effect. The reduction in energy barrier after carbonation/hydrogenation leads to the weakness of the first-order magnetic transition and the decrease in hysteresis [7,20].

Fig. 3 exhibits the magnetization isotherms (*M*–*H*) of $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ and $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}H_x$ ($x = 0$, 0.6 and 1.2), measured around T_C in the field ascending and descending processes. The *M*–*H* curve of $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ exhibits an obvious magnetic hysteresis, due to the field-induced itinerant electron metamagnetic (IEM) transition above T_C as observed in $La(Fe,Si)_{13}$ [21]. The addition of minor carbon causes a remarkable reduction of magnetic hysteresis (see Fig. 3(b)). The magnetic hysteresis loss, that is defined as the area enclosed by the two *M*–*H* curves for the field ascending and descending cycling, are about 93 and 12 J/kg for $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ and $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}$ under a field of 5 T, respectively. It is interesting to note that the magnetic hysteresis is almost zero for the samples of $x = 0.6$ and 1.2 (Fig. 3(c)), which is very useful for magnetic refrigeration applications. The Arrott plot of $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ as shown in Fig. 3(d), exhibits negative slope, confirming further the characteristic of first-order magnetic

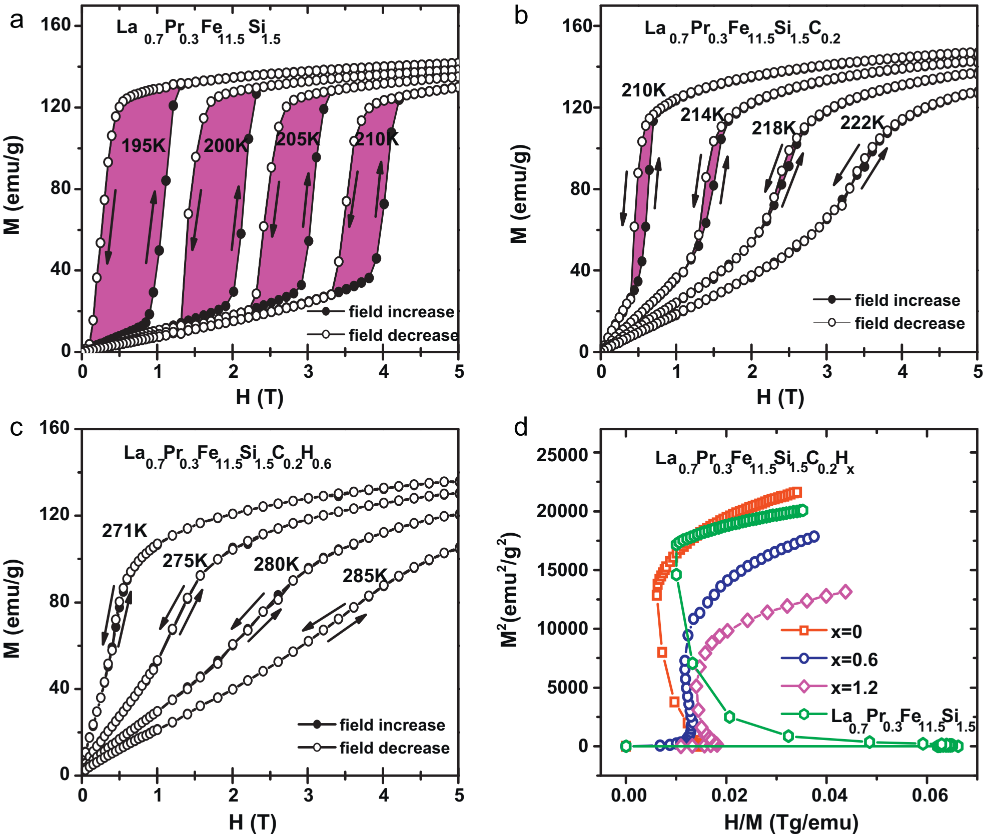

Fig. 3. Magnetization isotherms of $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ (a), $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}$ (b) and $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}H_{0.6}$ (c) measured on field increasing and decreasing. (d) Arrott plots for samples $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ and $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}H_x$ (x = 0, 0.6 and 1.2) at temperatures just above Curie temperature, respectively.

transition. However, the insertion of carbon and hydrogen leads to the declining of the negative slope, indicating the weakening of the first-order nature of the magnetic transition. However, the phase transition is still of the first-order in character after the carbonization or/and hydrogenation, which is favorable for the achievement of large ΔS_M.

The ΔS_M of $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}H_x$ is calculated based on the isothermal magnetization data by using the Maxwell relation $\Delta S_M = \int_0^H (\partial M/\partial T)_H dH$. Fig. 4 shows the ΔS_M as a function of temperature for magnetic field changes of 0–2 T and 0–5 T, respectively. For the samples with x = 0, 0.6 and 1.2, the maximal values of $-\Delta S_M$ are 25.6, 19.2 and 17.1 J/kg K for a field change of 0–2 T and 28.1, 24.7 and 22.1 J/kg K for a field change of 0–5 T. The large ΔS_M in $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}H_x$ is due to the field-induced IEM transition from PM to FM states above T_C. The asymmetric broadening of the ΔS_M peak toward high temperatures with magnetic field increasing is a typical character of the field-induced metamagnetic transition. The reduction of ΔS_M with x is due to the weakening of the IEM transition caused by interstitial carbon and hydrogen atoms. However, a large ΔS_M near the room temperature is still obtained in $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}H_{1.2}$. This indicates that the titled compound is a promising candidate for magnetic refrigerants. The RC value of $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}H_x$ compounds have also been calculated by using the approach suggested by Gschneidner et al. [22]. The RC is defined as $RC = \int_{T_1}^{T_2} |\Delta S_M| \, dT$, where T_1 and T_2 are the temperatures corresponding to both sides of the half-maximum value of ΔS_M peak, respectively. The estimated RC value for $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}H_{1.2}$ is 370 J/kg for a field change of 0–5 T.

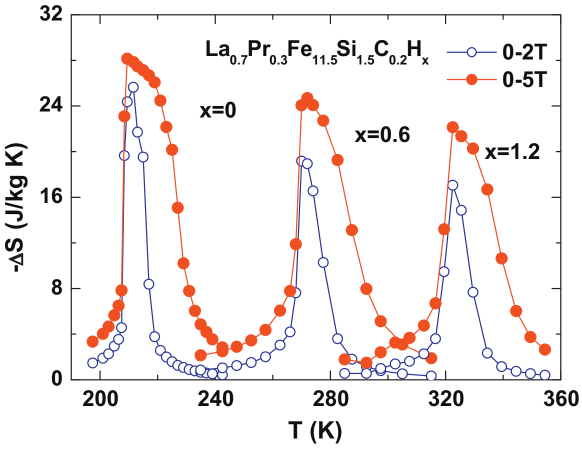

Fig. 4. Magnetic entropy change ΔS_M as a function of temperature for $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}H_x$ (x = 0, 0.6 and 1.2).

4. Conclusions

In conclusion, the addition of interstitial carbon atom in $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}H_x$ not only slows down hydrogen absorbing but also prevents hydrogen from being released, which is propitious for an accurate control of hydrogen content in magnetic refrigeration applications. The introduction of carbon and hydrogen atoms into $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ leads to an increase in T_C and a remarkable reduction in thermal/magnetic hysteresis while large ΔS_M is still maintained. A room temperature ΔS_M of 22.1 J/kg K with an RC value of 370 J/kg is obtained for a field change of 0–5 T. The advantages such as large reversible ΔS_M, considerable RC and almost zero hysteresis loss make $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}H_x$ a very promising candidate for magnetic refrigeration near room temperature.

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References

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

[2] E. Brück, in: K.H.J. Buschow (Ed.), Handbook of Magnetic Materials, vol. 17, Elsevier B.V, 2008, p. 235.

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

[4] F.X. Hu, B.G. Shen, J.R. Sun, X.X. Zhang, Chin. Phys. 9 (2000) 550.

[5] O. Tegus, E. Brück, K.H.J. Buschow, F.R. de Boer, Nature (Lond.) 415 (2002) 150.

[6] B.G. Shen, J.R. Sun, F.X. Hu, H.W. Zhang, Z.H. Cheng, Adv. Mater. 21 (2009) 4545.

[7] R.P. Santana, N.A. de Oliveira, P.J. von Ranke, J. Alloys Compd. 509 (2011) 6346.

[8] V. Provenzano, A.J. Shapiro, R.D. Shull, Nature (Lond.) 429 (2004) 853.

[9] F.X. Hu, B.G. Shen, J.R. Sun, G.J. Wang, Z.H. Cheng, Appl. Phys. Lett. 80 (2002) 826.

[10] J. Shen, B. Gao, L.Q. Yan, Y.X. Li, H.W. Zhang, F.X. Hu, J.R. Sun, Chin. Phys. 16 (2007) 3848.

[11] J. Shen, Y.X. Li, J. Zhang, B. Gao, F.X. Hu, H.W. Zhang, Y.Z. Chen, C.B. Rong, J.R. Sun, J. Appl. Phys. 103 (2008) 07B317.

[12] Y.F. Chen, F. Wang, B.G. Shen, G.J. Wang, J.R. Sun, J. Appl. Phys. 93 (2003) 1323.

[13] M. Balli, D. Fruchart, D. Gignoux, Appl. Phys. Lett. 92 (2008) 232505.

[14] Y.F. Chen, F. Wang, B.G. Shen, F.X. Hu, J.R. Sun, G.J. Wang, Z.H. Cheng, J. Phys. Condens. Matter 15 (2003) L161.

[15] A. Fujita, S. Fujieda, Y. Hasegawa, K. Fukamichi, Phys. Rev. B 67 (2003) 104416.

[16] S.M. Podgornykh, Y.V. Shcherbakova, Phys. Rev. B 73 (2006) 184421.

[17] J. Lyubina, K. Nenkov, L. Schultz, O. Gutfleisch, Phys. Rev. Lett. 101 (2008) 177203.

[18] M. Rosca, M. Balli, D. Fruchart, D. Gignoux, E.K. Hlil, S. Miraglia, B. Ouladdiaf, P. Wolfers, J. Alloys Compd. 490 (2010) 50.

[19] X.B. Liu, Z. Altounian, A.D. Beath, J. Appl. Phys. 95 (2004) 7067.

[20] J.L. Zhao, J. Shen, F.X. Hu, Y.X. Li, J.R. Sun, B.G. Shen, J. Appl. Phys. 107 (2010) 113911.

[21] A. Fujita, Y. Akamatsu, K. Fukamichi, J. Appl. Phys. 85 (1999) 4756.

[22] K.A. Gschneidner Jr., V.K. Pecharsky, A.O. Pecharsky, C.B. Zimm, Mater. Sci. Forum 315 (1999) 69.