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Effect of R substitution on magnetic properties and magnetocaloric effects of $La_{1-x}R_xFe_{11.5}Si_{1.5}$ compounds with R=Ce, Pr and Nd*

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Magnetic properties and magnetocaloric effects of $La_{1-x}R_xFe_{11.5}Si_{1.5}$ (R=Pr, ($0 \le x \le 0.5$); R = Ce and Nd, ($0 \le x \le 0.3$)) compounds are investigated. Partially replacing La with R = Ce, Pr and Nd in $La_{1-x}R_xFe_{11.5}Si_{1.5}$ leads to a reduction in Curie temperature due to the lattice contraction. The substitution of R for La causes an enhancement in field-induced itinerant electron metamagnetic transition, which leads to a remarkable increase in magnetic entropy change ΔS_m and also in hysteresis loss. However, a high effective refrigerant capacity RC_{eff} is still maintained in $La_{1-x}R_xFe_{11.5}Si_{1.5}$. In the present samples, a large ΔS_m and a high RC_{eff} have been achieved simultaneously.

Keywords: magnetocaloric effect, hysteresis loss, refrigerant capacity
PACC: 7530S, 7550C

1. Introduction

Earlier work reveals that $LaFe_{13-x}Si_x$ compounds have a high magnetization and low Curie temperature.[1,2] In a paramagnetic state above the Curie temperature T_C, $LaFe_{13-x}Si_x$ exhibits field-induced itinerant electron metamagnetic (IEM) transition behaviour.[3] It is found that the $LaFe_{13-x}Si_x$ compounds with a low Si concentration undergo a first-order magnetic transition at T_C and exhibit a large magnetic entropy change ΔS_m around T_C.[4,5] The families of $NaZn_{13}$-type (La, R) (Fe, M)$_{13}$ with the first-order magnetic transition such as interstitial compounds LaFeSiH[6,7] and LaFeSiC[8] as well as the compounds with partial substitutions of R=Ce,[9] and M=Mn[10] or Co,[11–13] etc for La and Fe have been systematically studied as attractive candidates for magnetic refrigerant materials. However, recent study has shown that[14–16] the hysteresis loss is inevitable for the materials with a first-order magnetic transition, which makes magnetic refrigeration less efficient. A material with a large ΔS_m does not necessarily have a large refrigeration efficiency. To improve the efficiency of magnetic refrigeration, it is important to enhance the refrigerant capacity (RC) and to reduce the hysteresis loss. Recently, the magnetocaloric effect (MCE) of the $NaZn_{13}$-type LaRFeSi (R=Ce, Pr and Nd) compounds was studied.[17–19] It has been found that partial substitution of R for La enhances the MCE in the $LaFe_{13-x}Si_x$ compounds due to the enhancement of the IEM transition behaviour.[17–19] Most investigations have been focused on the improvement of ΔS_m for the $LaFe_{13-x}Si_x$ compounds by substituting R atoms for La, while both the hysteresis loss and the RC are little studied. Recently, we have also investigated magnetic properties and magnetic entropy changes in $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$.[20] In the present paper, we report on the effect of the substitution of R on magnetic entropy change, hysteresis loss and refrigerant capacity in $La_{1-x}R_xFe_{11.5}Si_{1.5}$ compounds with R=Ce, Pr and Nd.

2. Experimental details

$La_{1-x}Ce_xFe_{11.5}Si_{1.5}$ (x = 0, 0.1, 0.2 and 0.3), $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ (x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) and $La_{1-x}Nd_xFe_{11.5}Si_{1.5}$ (x = 0, 0.1, 0.2 and 0.3) compounds were prepared by arc melting appropriate amounts of the raw materials of Pr (99% in purity), La, Ce and Nd (99.9%), Fe (99.9%), and Si (99.999%)

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in a high-purity argon atmosphere. The sample was turned over and remelted several times to ensure homogeneity. The as-prepared ingots were wrapped with Mo foil, sealed in a quartz tube of high vacuum, annealed at 1373 K for 40 days and then quenched in liquid nitrogen. X-ray diffraction (XRD) measurements on powder samples were performed by using Cu Kα radiation to identify phase structure and crystal structure. The magnetization was measured as a function of temperature and magnetic field around Curie temperature by using a physical property measurement system (PPMS) from Quantum Design and a superconducting quantum interference device (SQUID) magnetometer.

3. Results and discussion

All the compounds studied here are of single phase with a cubic $NaZn_{13}$-type structure (space group $Fm\bar{3}c$). The temperature dependence of the magnetization of $La_{1-x}R_xFe_{11.5}Si_{1.5}$ (R=Ce, Pr and Nd) compounds have been measured under a low magnetic field of 0.01 T. Figure 1(a) shows an example of the thermomagnetic M–T curves measured during heating and cooling for $La_{0.6}Pr_{0.4}Fe_{11.5}Si_{1.5}$. Our study shows that the M–T curves for $La_{1-x}R_xFe_{11.5}Si_{1.5}$ have a large thermal hysteresis. The thermal hysteresis is estimated from the difference in temperature of magnetic transition between during cooling and during heating and its value increases with the increase of R concentration. The thermal hystereses are found to be about 1.4, 3.2 and 5 K for $LaFe_{11.5}Si_{1.5}$ (x = 0), $La_{0.7}Nd_{0.3}Fe_{11.5}Si_{1.5}$ and $La_{0.5}Pr_{0.5}Fe_{11.5}Si_{1.5}$, respectively. This implies that the substitution of R for La in $LaFe_{11.5}Si_{1.5}$ can enhance thermal-induced first-order magnetic transition at T_C.

Figure 1(b) shows the thermomagnetic M–T curves in a field of 0.01 T for $LaFe_{11.5}Si_{1.5}$ ($x = 0$) and $La_{0.7}R_{0.3}Fe_{11.5}Si_{1.5}$ (R=Ce, Pr and Nd) compounds. The Curie temperatures T_C for $La_{1-x}R_xFe_{11.5}Si_{1.5}$ are determined from the heating M–T curves and their values are shown in Fig.2(a). The T_C is found to decrease monotonically with the increase of R concentration. A similar result has been observed in other $NaZn_{13}$-type LaRFeSi compounds.[17–19] The Curie temperatures of rare-earth (R) transition-metal (T) compounds are determined by the T–T, the R–T, and the R–R interactions. Generally, the T–T interaction is dominant but the R–R interaction is negligible. For $LaFe_{11.5}Si_{1.5}$, the Curie temperature is determined only by the contributions of the Fe–Fe interaction because La is nonmagnetic. In the $La_{1-x}R_xFe_{11.5}Si_{1.5}$ compounds, the Curie temperature is determined mainly by the Fe–Fe and the R–Fe exchange interactions. Figure 2(b) shows a relation between the T_C and the unit-cell volume for $La_{1-x}R_xFe_{11.5}Si_{1.5}$. The T_C exhibits a monotonic reduction with the decrease of the unit-cell volume, at a rate of $\sim 2990\,\mathrm{K/nm^3}$ for $La_{1-x}Ce_xFe_{11.5}Si_{1.5}$, $\sim 1450\,\mathrm{K/nm^3}$ for $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ and $\sim 800\ \mathrm{K/nm^3}$ for $La_{1-x}Nd_xFe_{11.5}Si_{1.5}$. The difference in T_C between La and R compounds with the same phase volumes indicates different contributions of the R–Fe exchange interactions, the contribution of Nd–Fe interaction > contribution of Pr–Fe interaction > contribution of Ce–Fe interaction for $La_{1-x}R_xFe_{11.5}Si_{1.5}$. Some investigations on the relation between unit-cell volume and Curie temperature for $LaFe_{13-x}Si_x$ based compounds,[6–8,10,17,18,21] have verified that the introduction of interstitial hydrogen or carbon can cause T_C to increase through expanding the lattice of the

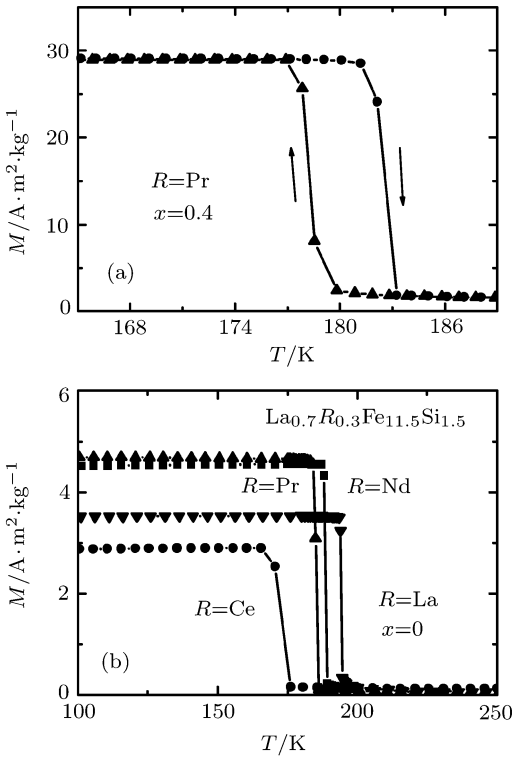


Fig.1. Thermomagnetic M–T curves measured during heating and cooling for $La_{0.6}Pr_{0.4}Fe_{11.5}Si_{1.5}$ under a magnetic field of 0.05 T (a) and M–T curves measured during heating for $LaFe_{11.5}Si_{1.5}$ ($x = 0$) and $La_{0.7}R_{0.3}Fe_{11.5}Si_{1.5}$ (R=Ce, Pr and Nd) compounds (b) under a magnetic field of 0.01 T.

compounds,[6−8,10,17] while the application of a static pressure can lead T_C to reduce through compressing the lattice.[22,23] A linear relation between T_C and atom spacing has been established by using the Bean–Rodbell model.[24] Therefore, it is apparent that the lattice contraction caused by the substitution of R for La leads to a reduction in T_C for $La_{1-x}R_xFe_{11.5}Si_{1.5}$.

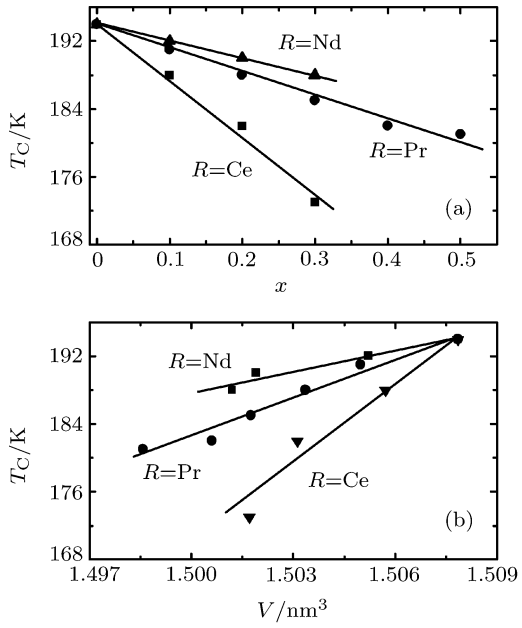


Fig.2. Curie temperature T_C as a function of R concentration (a) and T_C as a function of unit-cell volume (b) for $La_{1-x}R_xFe_{11.5}Si_{1.5}$ compounds with R=Ce, Pr and Nd.

We have measured the magnetization isotherms of $La_{1-x}R_xFe_{11.5}Si_{1.5}$ under an ascending magnetic field and descending magnetic fields in a wide temperature range around the Curie temperature. The sweep rate of the field is slow enough to ensure that the M–H curves are recorded in an isothermal process. As an example, Fig.3 shows the curves for typical magnetization versus magnetic field for $La_{1-x}Nd_xFe_{11.5}Si_{1.5}$ (x = 0.1, 0.2 and 0.3). In an isothermal process of magnetization, the magnetic entropy change of the materials can be derived from Maxwell relation by integrating the magnetization M over the magnetic field H, i.e.

$$\Delta S_m(T,H) = S_m(T,H) - S_m(T,0) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H. \quad (1)$$

To derive the temperature dependence of magnetic entropy change, the following numerical approximation of the integral is usually adopted:

$$|\Delta S_m| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i}\Delta H_i, \quad (2)$$

where M_i and M_{i+1} are the experimental values of the magnetization measured at T_i and T_{i+1} in an applied magnetic field H_i, respectively. The ΔS_m for $La_{1-x}R_xFe_{11.5}Si_{1.5}$ are calculated from the isothermal magnetization curves according to expression (2). The R concentration dependence of ΔS_m is shown in Fig.4, in which the value of ΔS_m is found to increase remarkably with the increase of R content from 23.7 J/(kg·K) for x = 0 to 32.4 J/(kg·K) for $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ (x = 0.5) and to 32.0 J/(kg·K) for $La_{1-x}Nd_xFe_{11.5}Si_{1.5}$ (x = 0.3). Large magnetic entropy change near T_C for $La_{1-x}R_xFe_{11.5}Si_{1.5}$ results from the field induced IEM transition.[17−20]

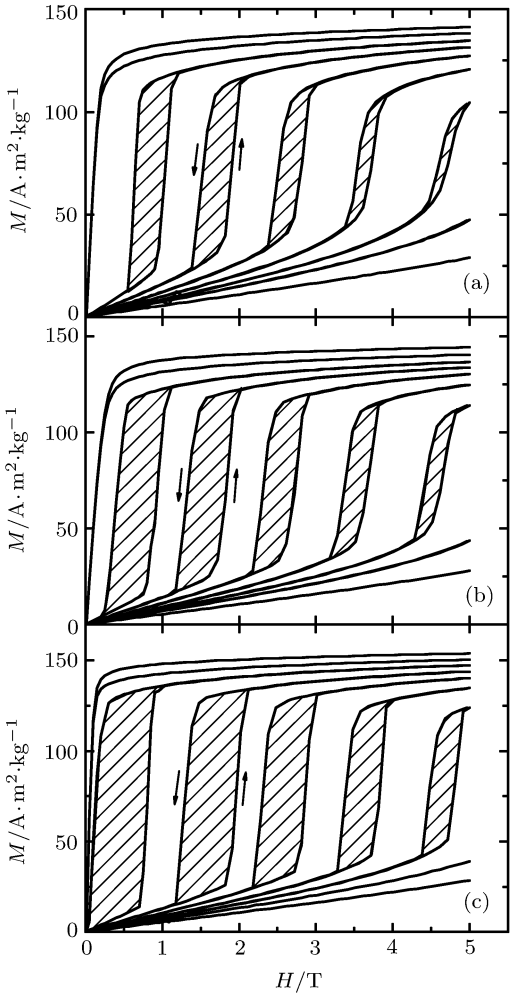


Fig.3. Isothermal magnetization curves measured under ascending and descending magnetic fields around the Curie temperature for $La_{1-x}Nd_xFe_{11.5}Si_{1.5}$ (x = 0.1 (a), 0.2 (b) and 0.3 (c)) compounds.

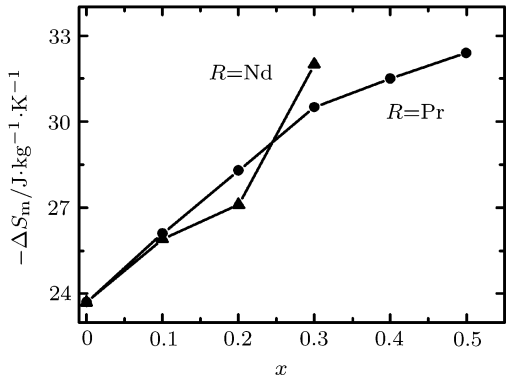


Fig.4. Magnetic entropy change as a function of R concentration for $La_{1-x}R_xFe_{11.5}Si_{1.5}$ compounds with R=Pr and Nd.

For each sample under the present study, it is observed that the magnetization measured in the first half of the loop shows a distinct magnetic transition with the increase of magnetic field in the vicinity of its T_C. The M–H loops clearly show that this field-induced phase transition reverses as field reduces, but with a large hysteresis in the transition field. The magnetic transition occurs at higher magnetic fields with the increase of temperature. It has been verified that this transition is associated with a field-induced IEM transition from paramagnetic to ferromagnetic state above T_C,[16,20,25] indicative of the nature of first-order magnetic transition in $La_{1-x}R_xFe_{11.5}Si_{1.5}$. The previous study indicates that materials undergoing a temperature and magnetic field induced first order transition often give rise to a large ΔS_m, but bring about some thermal and magnetic hystereses as well. For example, the $Gd_5Si_2Ge_2$ compound has simultaneously a large ΔS_m of 20 J/(kg·K) and a hysteresis loss of about 65 J/kg in the vicinity of its T_C due to a magnetic field induced crystallographic structural change from the high-temperature monoclinic paramagnetic phase to the low-temperature orthorhombic ferromagnetic phase.[14] A large ΔS_m and hysteresis loss were also observed in $Ni_{50}Mn_{34}In_{16}$ around the austenite-martensite transition.[26] The magnetic hysteresis loops in the M–H curves near T_C illustrate the hysteresis loss. For $La_{1-x}R_xFe_{11.5}Si_{1.5}$ (R=Pr and Nd), the temperature dependences of hysteresis loss, which are determined by calculating the area enclosed by the ascending and descending branches of M–H loops, are shown in Fig.5. The hysteresis loss for $La_{1-x}R_xFe_{11.5}Si_{1.5}$ is found to reach a maximum around T_C. Figure 6 shows the R-content dependence of maximum hysteresis loss, which is found to increase with the increase of R concentration for $La_{1-x}R_xFe_{11.5}Si_{1.5}$. Because the large hysteresis loss results from the field-induced IEM transition in compounds with first-order magnetic transition,[20,25] this increase in hysteresis loss also indicates that the increase in substitution of R content in $La_{1-x}R_xFe_{11.5}Si_{1.5}$ leads to the enhancement of IEM transition.

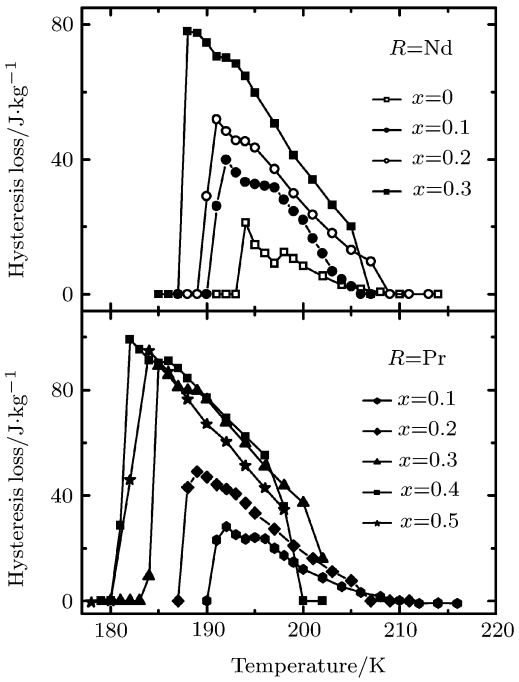


Fig.5. Hysteresis losses as a function of temperature for $La_{1-x}Nd_xFe_{11.5}Si_{1.5}$ (x = 0, 0.1, 0.2 and 0.3) compounds (a) and $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ (x = 0.1, 0.2, 0.3, 0.4 and 0.5) compounds (b).

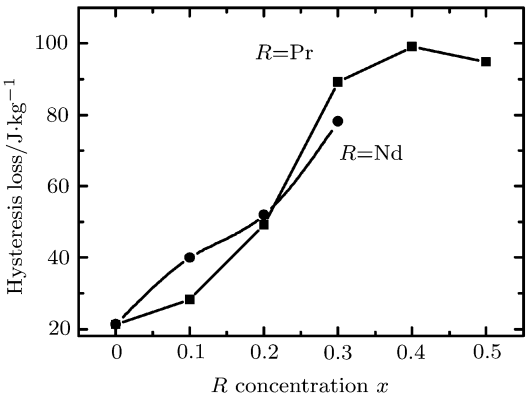


Fig.6. Maximum values of hysteresis loss as a function of R concentration for $La_{1-x}R_xFe_{11.5}Si_{1.5}$ compounds with R = Pr and Nd.

As an example, Figure 7 shows the temperature dependence of the ΔS_m for $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ compound with field increasing from 0 to 5 T. From the curves for ΔS_m versus temperature for $La_{1-x}R_xFe_{11.5}Si_{1.5}$ compounds, the values of RC are calculated by numerically integrating the area

under the ΔS_m–T curve, with the temperatures at half maximum of the peak used as the integration limits.[27] The maximum values of RC range from 428 to 528 J/kg for a field change of 0–5 T. Although the $La_{1-x}R_xFe_{11.5}Si_{1.5}$ compounds exhibit high RC values, they also have a large hysteresis loss, which can reduce the MCE of the refrigerant material. An effective refrigerant capacity (RC_{eff}), the hysteresis losses are much subtracted from the calculated RC. The maximum values of RC_{eff} for a field change of 0–5 T are found to range from 407 to 454 J/kg for

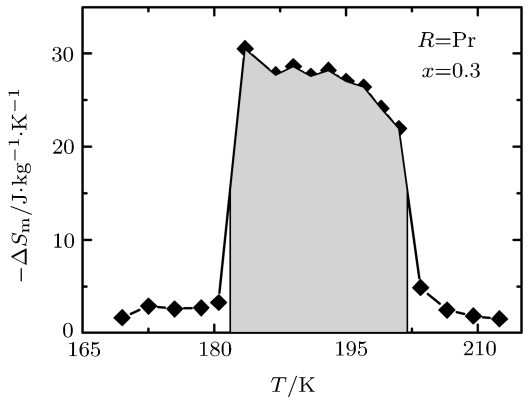


Fig.7. Magnetic entropy change of the $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ compound as a function of temperature for a magnetic field change of 0–5 T, where RC is also shown as a shaded area.

$La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ as x varies from 0 to 0.5, and from 407 to 465 J/kg for $La_{1-x}Nd_xFe_{11.5}Si_{1.5}$ as x increases from 0 to 0.3. For the present samples, large values of RC_{eff} and ΔS_m have been simultaneously achieved, which are advantageous to the practical application of the materials in a corresponding temperature range.

4. Conclusions

Magnetic and magnetocaloric properties of $La_{1-x}R_xFe_{11.5}Si_{1.5}$ compounds with R=Ce, Pr and Nd are investigated by magnetization measurement. Substitution of R for La in $LaFe_{11.5}Si_{1.5}$ can enhance the field-induced IEM transition and results in a large ΔS_m and hysteresis loss. The maximum value of ΔS_m for a field change of 0–5 T is found to increase from 23.7 J/(kg·K) for $x = 0$ to 32.4 J/(kg·K) for $x = 0.5$ in $La_{1-x}R_xFe_{11.5}Si_{1.5}$ and to 32.0 J/(kg·K) for $x = 0.3$ in $La_{1-x}Nd_xFe_{11.5}Si_{1.5}$, the corresponding change of the maximum hysteresis loss is from 21.2 J/kg to 99.1 J/kg for R=Pr and to 77.5 J/kg for R=Nd. The effective refrigerant capacity (RC_{eff}) still reaches 407–465 J/kg under a field change from 0 to 5 T. Our present study reveals that a large ΔS_m and a high RC_{eff} can be simultaneously achieved in $La_{1-x}R_xFe_{11.5}Si_{1.5}$ compounds.

References

[1] Buschow K H J 1977 *Rep. Progr. Phys.* **40** 1179
[2] Palstra M T T, Nieuwenhuys G J, Mydosh J A and Buschow K H J 1985 *Phys. Rev.* B **31** 4622
[3] Fujita A, Akamatsu Y and Fukamichi K 1999 *J. Appl. Phys.* **85** 4756
[4] Hu F X, Shen B G, Sun J R and Zhang X X 2000 *Chin. Phys.* **9** 550
[5] Hu F X, Shen B G, Sun J R, Chen Z H, Rao G H and Zhang X X 2001 *Appl. Phys. Lett.* **78** 3675
[6] Chen Y F, Wang F, Shen B G, Hu F X, Cheng Z H, Wang G J and Sun J R 2002 *Chin. Phys.* **11** 741
[7] Fujita A, Fujieda S, Hasegawa Y and Fukamichi K 2003 *Phys. Rev.* B **67** 104416
[8] Chen Y F, Wang F, Shen B G, Wang G J and Sun J R 2003 *J. Appl. Phys.* **93** 1323
[9] Fujieda S, Fujita A and Fukamichi K 2006 *J. Alloys Compd.* **408** 1165
[10] Wang F, Chen Y F, Wang G J, Sun J R and Shen B G 2003 *Chin. Phys.* **12** 911
[11] Hu F X, Shen B G, Sun J R, Wang G J and Cheng Z H 2002 *Appl. Phy. Lett.* **80** 826
[12] Yan A, Muller K H and Gutfleisch O 2008 *J. Alloys Compd.* **450** 18
[13] Balli M, Fruchart D and Gignoux D 2008 *Appl. Phys. Lett.* **90** 232505
[14] Provenzano V, Shapiro A J and Shull R D 2004 *Nature* (London) **429** 853
[15] de Campos A, Rocco D L, Carvalho A M G, Caron L, Coelho A A, Gama S, da Silva L M, Gandra F V C G, Santos A O D, Cardoso L P, von Ranke P J and de Oliveira N A 2006 *Nature Materials* **5** 802
[16] Shen J, Gao B, Zhang H W, Hu F X, Li Y X, Sun J R and Shen B G 2007 *Appl. Phy. Lett.* **91** 142504
[17] Fujieda S, Fujita A and Fukamichi K 2007 *J. Appl. Phys.* **102** 023907
[18] Fujieda S, Fujita A, Fukamichi K, Hirano N and Nagaya S 2006 *J. Alloys Compd.* **408** 1165
[19] Kim Anh D T, Thuy N P, Duc N H, Nhien T T and Nong N V 2003 *J. Magn. Magn. Mat.* **262** 427
[20] Shen J, Gao B, Yan L Q, Li Y X, Zhang H W, Hu F X and Sun J R 2007 *Chin. Phys.* **16** 3848
[21] Jia L, Sun J R, Shen J, Dong Q Y, Hu F X, Zhao T Y and Shen B G 2008 *Appl. Phys. Lett.* **92** 182503
[22] Sun Y, Arnold Z, Kamarad J, Wang G J, Shen B G and Cheng Z H 2006 *Appl. Phys. Lett.* **89** 172513
[23] Jia L, Sun J R, Shen B G, Li D X and Nimori S 2007 *J. Appl. Phys.* **101** 106108
[24] Bean C P and Rodbell D S 1962 *Phys. Rev.* **162** 104
[25] Shen J, Li Y X, Zhang J, Gao B, Hu F X, Zhang H W, Chen Y Z, Rong C B, Sun J R 2008 *J. Appl. Phys.* **103** 07B317
[26] Chattopadhyay M K, Sharma V K and Roy S B 2008 *Appl. Phys. Lett.* **92** 022503
[27] Gschneidner K A Jr, Pecharsky V K, Pecharsky A O and Zimm C B 1999 *Mater. Sci. Forum* **315** 69