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Realization of a small hysteresis loss and a large magnetic entropy change in NaZn$_{13}$-type La–Fe–Si compound

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A B S T R A C T

In NaZn$_{13}$-type $Pr_zLa_{1-z}(Fe_{1-y}Co_y)_{11.8}Si_{1.2}$ ($0.07 < y < 0.09$, $z = 0$–0.4) compound, besides adjusting the phase transition temperature to room temperature after the substitutions of Pr for La and Co for Fe, the character of magnetic first-order phase transition is strongly reduced. Thus, the hysteresis losses hardly exist in these compounds. Meanwhile, a large magnetic entropy change about 13.6–15.7 J/(kg K), superior to that of Gd, is obtained in 0–5 T field change. So, these compounds are suitable candidates for magnetic refrigerant near room temperature.

1. Introduction

Since the discovery of the giant magnetocaloric effect (MCE) in $Gd_5Si_2Ge_2$ [1], much interest has been focused on the magnetic refrigeration near room temperature based on the MCE due to its numerous potential advantages over vapor-compression refrigeration [2–4]. The isothermal magnetic entropy change (ΔS) is an important parameter for evaluating the refrigerant properties [5]. Currently, large MCE has been found in materials with a magnetic first-order phase transition (FOPT), such as the $R_5(Si, Ge)_4$ [1,4], MnAs [6,7], La(Fe, Si)$_{13}$ [8,9], MnFe(P, As) [3] and Ni$_2$MnGa [10]-based compounds. Magnetic refrigeration Ericson cycle which is composed of two isothermal and two isofield processes is very suitable for high-temperature magnetic refrigeration because the lattice entropy can be counteracted during the two isofield processes [11]. However, large hysteresis losses, which make magnetic refrigeration less efficient in Ericson cycle, always exist in the strong FOPT.

We note that the way to reduce hysteresis losses is reported in $Gd_5Ge_2Si_2$ by the addition of iron [12]. $Gd_5Ge_2Si_2$ with iron addition is composed of a dominant matrix phase and a minor phase located along the grain boundaries of the matrix phase. The main effect of the iron addition in $Gd_5Ge_2Si_2$ compound is to suppress the field-induced FOPT, resulting in much smaller hysteresis losses [12]. In this work, we will report the realization of reduction of hysteresis losses in magnetic refrigerant $LaFe_{11.8}Si_{1.2}$-based compound with a cubic NaZn$_{13}$-type structure. The mechanism to reduce the hysteresis losses in this work is different from that in $Gd_5Ge_2Si_2$ with iron addition.

With the increase of Fe concentration in La(Fe, Si)$_{13}$ compounds, the MCE is greatly enhanced and the nature of phase transition changes from the second-order to the FOPT. The character of a FOPT, i.e. the reduced difference of spontaneous magnetization between ferromagnetic and paramagnetic states, is strengthened by further increasing the Fe content [13]. Simultaneously, Curie temperature T_C becomes much lower than room temperature [8, 9,14,15]. However, the low Curie temperature can easily be elevated by the substitution of Co for Fe [16]. Furthermore, Co addition in Fe-based alloys enhances their magnetic moments [17]. The magnetic moments in La(Fe, Si)$_{13}$ compound can also be improved by the substitution of Pr for nonmagnetic La. The enhancement of magnetic moments is necessary to obtain a large ΔS [18,19]. The hydrogenation can also adjust T_C to room temperature and a large magnetic entropy change has been obtained. However, its hydrides show the large hysteresis losses and are instable at high temperature. The hysteresis losses in melt-spun ribbons $LaFe_{11.57}Si_{1.43}$ are much smaller than those in as-annealed bulk alloys which have the same nominal Si content as the former [20]. In fact, the smaller

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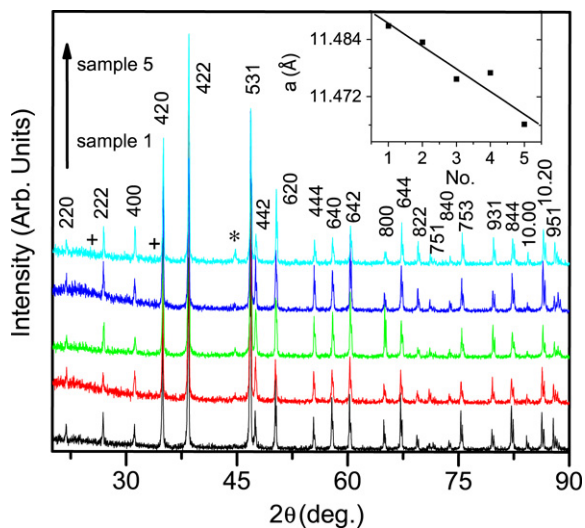*E-mail address:* hwzhang@aphy.iphy.ac.cn (H.W. Zhang).

Fig. 1. X-ray diffraction patterns for $Pr_zLa_{1-z}(Fe_{1-y}Co_y)_{11.8}Si_{1.2}$ compounds at room temperature, marked by "*" and "+" are the impurity of α-Fe and $LaSi_2$ phases, respectively. As an example, Miller indexes of Sample 5 are displayed. The inset represents the lattice parameter of all the studied samples.
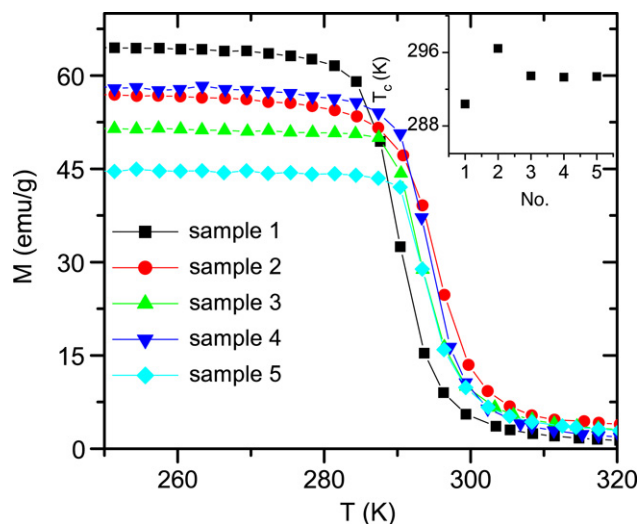
Table 1
Composition of the studied $Pr_zLa_{1-z}(Fe_{1-y}Co_y)_{11.8}Si_{1.2}$ compounds

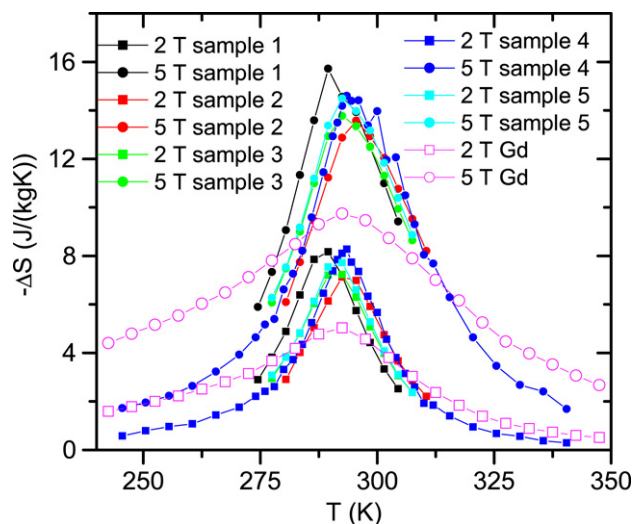| Alloy	1	2	3	4	5
y	0.075	0.08	0.08	0.085	0.085
z	0	0.1	0.2	0.3	0.4

Fig. 3. Temperature dependence of magnetic entropy change in field changes of 0–2 T and 0–5 T for $Pr_zLa_{1-z}(Fe_{1-y}Co_y)_{11.8}Si_{1.2}$ compounds (closed symbols), compared with that of Gd (open symbols).

Fig. 2. Temperature dependence of magnetization in a field of 0.1 T for $Pr_zLa_{1-z}(Fe_{1-y}Co_y)_{11.8}Si_{1.2}$ compounds. The inset shows T_C of all the studied samples.

hysteresis losses in melt-spun ribbons can be understood by considering the preparation method of ribbons. Namely, there is inhomogeneity in the component and the existence of a small amount of α-Fe in the melt-spun ribbons, which leads to the formation of La(Fe, Si)$_{13}$ compound with Si content higher than that in the nominal compound.

In Ref. [16], the substitution of Co for Fe in La(Fe, Si)$_{13}$ compounds can easily increase T_C and greatly decrease the hysteresis losses but decrease ΔS. While in Ref. [18], Pr substitution increases saturation magnetization and ΔS but decreases T_C. In order to obtain refrigerant materials with a large ΔS near room temperature, we investigate La(Fe, Si)$_{13}$ compounds with the proper substitutions of Pr for La and Co and Fe.

2. Experimental

The samples with nominal composition $Pr_zLa_{1-z}(Fe_{1-y}Co_y)_{11.8}$ Si$_{1.2}$ ($0.07 < y < 0.09, z = 0, 0.1, 0.2, 0.3, 0.4$, see Table 1) were prepared by arc melting the starting materials with purity

of 99.9 wt%. The weight loss for each sample is less than 0.1% after melting. The ingots were subsequently homogenized in a vacuum-sealed quartz tube for 2 months at 1373 K. The structure of the samples was characterized using x-ray powder diffraction (XRD). Magnetic measurements were carried out using a superconducting quantum interference device magnetometer. The value of ΔS was evaluated from the magnetization data by using the Maxwell relationship.

3. Results and discussion

XRD patterns at room temperature (Fig. 1) show that the main phase in all the samples is of cubic NaZn$_{13}$-type structure. LaCo$_{13}$ is the only stable one in all the binary R–M (M = Fe, Co, Ni) compounds with NaZn$_{13}$-type structure. LaFe$_{13}$ with NaZn$_{13}$-type structure does not exist. However, the proper substitution of the third element such as Si and Al for Fe is necessary to form NaZn$_{13}$-type structure. In other words, it is easy for α-Fe to separate out of La(Fe, Si)$_{13}$ compound. A small amount of α-Fe and LaSi$_2$ is found in the samples as impurity phases [15]. They are marked by "*" and "+" in the pattern of an example sample 5, respectively. The inset of Fig. 1 indicates that the lattice parameter a decreases from 11.486 Å for sample 1 to 11.466 Å for sample 5, which is due to the smaller atomic radius of the substitution Pr and Co.

Fig. 2 exhibits the temperature dependence of the magnetization of $Pr_zLa_{1-z}(Fe_{1-y}Co_y)_{11.8}Si_{1.2}$ compounds in a field of 0.1 T. T_C, determined as the temperature corresponding to the minimum in dM/dT, is around room temperature for the present samples. It is 290, 296, 294, 293, and 293 K for the samples 1–5, respectively, which is shown in the inset of Fig. 2.

Fig. 3 displays the temperature dependence of ΔS in 0–2 T and 0–5 T field changes for all the samples, in comparison with that of the pure Gd. The maximum magnetic entropy change $-\Delta S_{max}$ in 0–5 T field changes for the samples 1–5 is 15.7, 13.6, 13.8, 14.6, and 14.5 J/(kg K), respectively, which notably exceeds that of Gd metal (9.7 J/(kg K)).
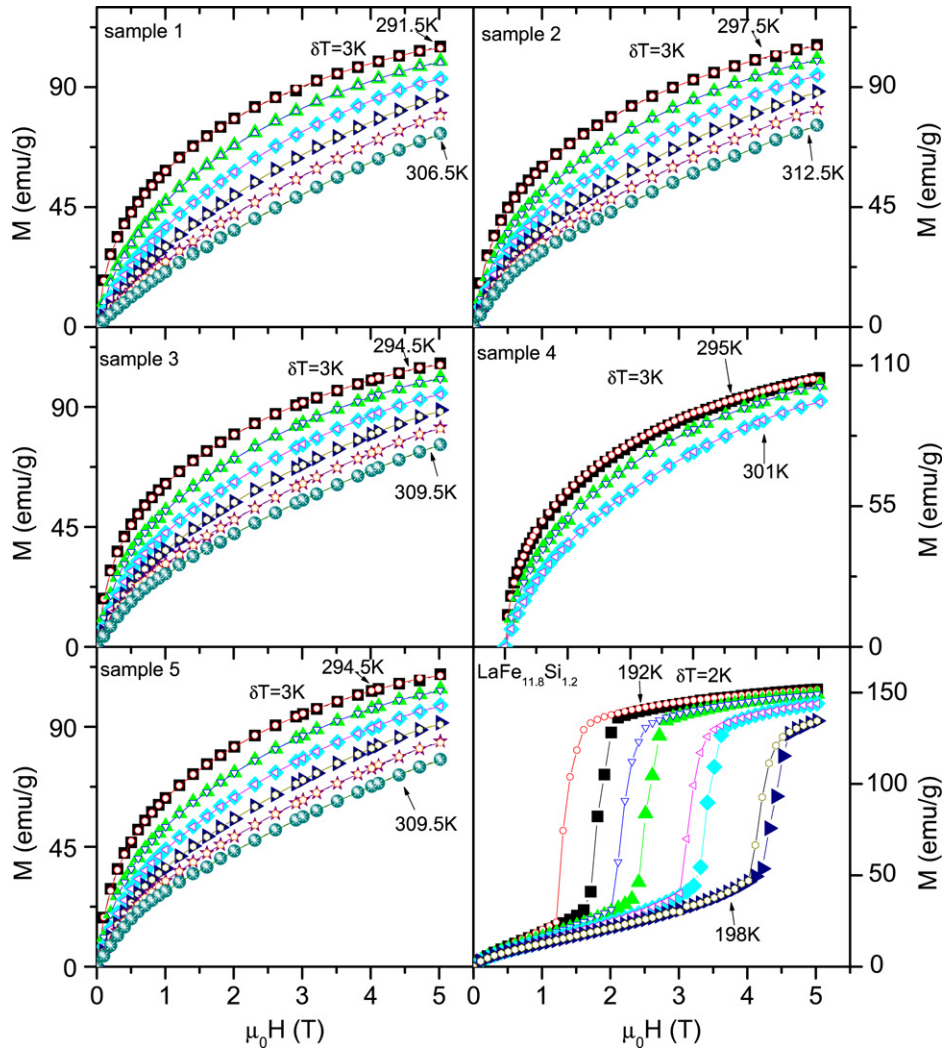
Fig. 4. Magnetization versus field curves for $Pr_zLa_{1-z}(Fe_{1-y}Co_y)_{11.8}Si_{1.2}$ compounds just above T_C and those for $LaFe_{11.8}Si_{1.2}$ compound (closed symbols for increasing field, and open symbols for decreasing field).

The hysteresis losses, which are very harmful to magnetic refrigeration Ericsson cycle, are determined by computing the area inside each magnetization versus field loop. Fig. 4 shows the hysteresis loops at several temperatures above T_C (1–16 K higher than T_C) for all the present samples as well as their parent alloy $LaFe_{11.8}Si_{1.2}$ ($T_C = 189$ K). It is obvious that the present samples have scarcely any hysteresis losses. However, the hysteresis losses are very large for $LaFe_{11.8}Si_{1.2}$ (54.1 J/kg at 192 K, 3 K higher than T_C). Thus, the present compounds are very attractive for magnetic refrigeration near room temperature.

As shown in Fig. 3, the peaks in different field changes for every sample nearly appear at their respective T_C, which means that the nature of the phase transition may be second-order or weak first-order. Fig. 5 displays the Arrott plots of all the present samples and $LaFe_{11.8}Si_{1.2}$ compound. The evidence for typical FOPT, such as a negative slope or an obvious inflection point [21,22], is not observed in the Arrott plots for all the present samples. In contrast, this is very clear for $LaFe_{11.8}Si_{1.2}$ compound.

The linear relationship between $-\Delta S_{max}$ and $H^{2/3}$ is first predicted by Oesterreicher and Parker [23]. Recently, the relationship is discussed intensively by the renormalized group theory and verified by the experimental results [24]. In order to find out the dependence of MCE on the applied field for the present samples, the value of $-\Delta S_{max}$ as a function of $h^{2/3}$ ($h = \frac{\mu_0\mu_B H}{k_B T_C}$) is plotted in Fig. 6. It

can be well fitted by eq. (5) in Ref. [24]. The value of parameters $-S(0, 1)$ defined in Ref. [24] is 339, 287, 294, 310, and 313 J/(kg K) for the samples 1–5, respectively. The value of $S(0, 0)$ is -1.22, -0.93, -1.01, -0.61, and -1.15 J/(kg K), successively. Obviously, $S(0, 0)$ is negative as mentioned in Ref. [24]. However, there is no linear relationship between $-S(0, 1)$ and $M_S(0)$ as pointed out in Ref. [24] for second-order transition materials. Associating with the results of Arrott plots, we can conclude that the nature of the phase transition is weak first-order.

In La(Fe, Si)$_{13}$ compound, La and Fe can be replaced by Pr and Co, respectively, where the addition of Pr and Co enters into the NaZn$_{13}$ structure. This is different from the case of the iron addition to Gd$_5$Ge$_2$Si$_2$ in which the addition of Fe leads to the formation of the grain boundary phase rich in Fe [12]. On the one hand, the character of FOPT is weakened by the Co substitution in La(Fe, Si)$_{13}$ compound, consistent with the recent report [16]. On the other hand, the existence of a small amount of α-Fe leads to the formation of $Pr_zLa_{1-z}(Fe_{1-y}Co_y)_{11.8}Si_{1.2}$ compound with Si content higher than that in the nominal compound, which also makes the character of FOPT weak. A weak FOPT around room temperature is realized using the proper Pr and Co substitutions. It is the weak FOPT that gives rise to the reduction of hysteresis losses in the magnetic refrigerant La(Fe, Si)$_{13}$.

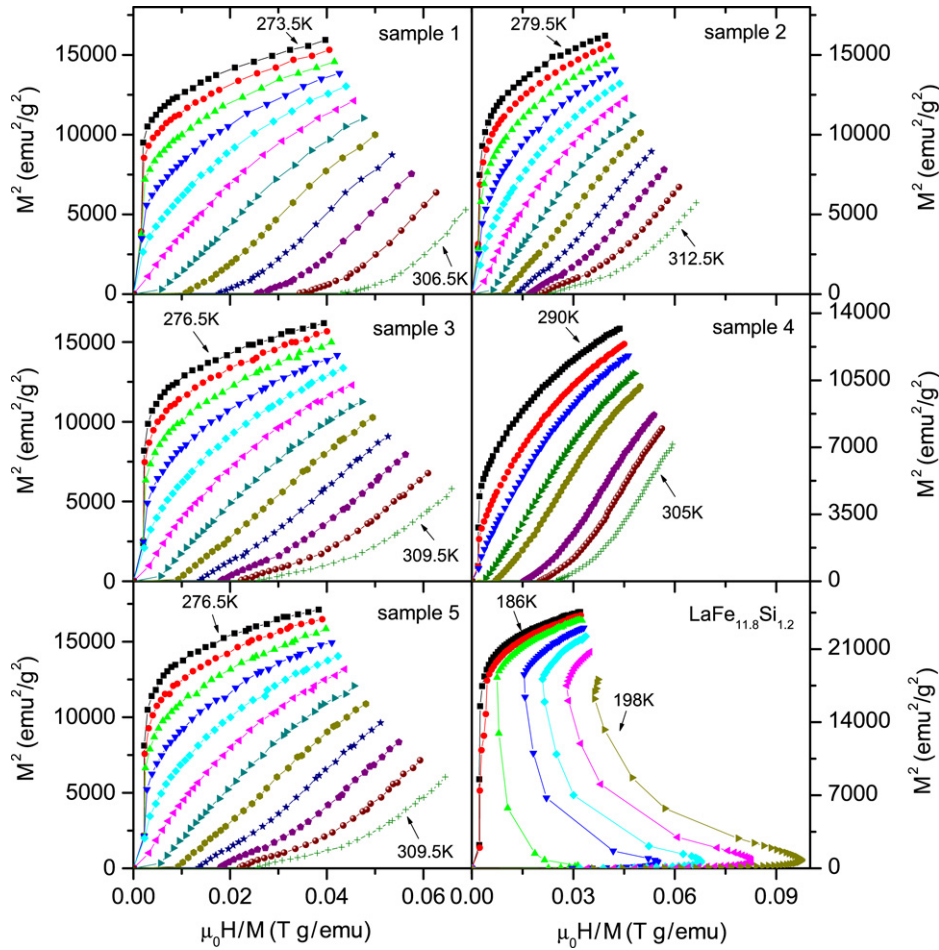**Fig. 5.** Arrott plots near T_C for $Pr_zLa_{1-z}(Fe_{1-y}Co_y)_{11.8}Si_{1.2}$ compounds as well as $LaFe_{11.8}Si_{1.2}$ compound.

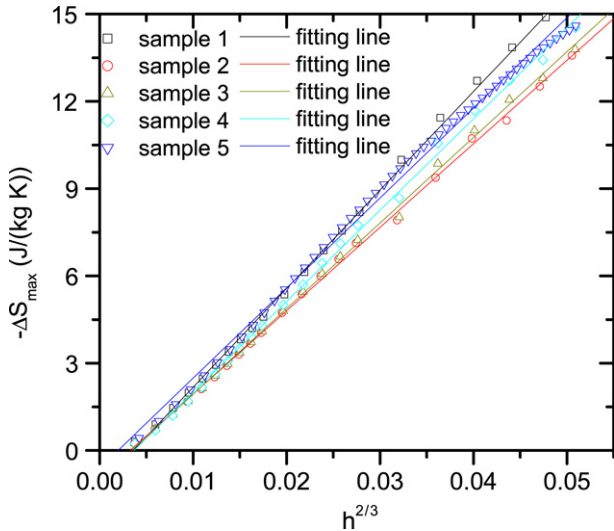**Fig. 6.** Maximum isothermal magnetic entropy change as a function of $h^{2/3}$ at T_C for $Pr_zLa_{1-z}(Fe_{1-y}Co_y)_{11.8}Si_{1.2}$ compounds (open squares), the solid line is the fitting one according to eq. (5) in Ref. [24].

4. Conclusions

In summary, near room temperature a large $-\Delta S_{max}$ about 13.6–15.7 J/(kg K) in 0–5 T field change, compared to 9.7 J/(kg K) for pure Gd metal, is obtained in $Pr_zLa_{1-z}(Fe_{1-y}Co_y)_{11.8}$ $Si_{1.2}$ compounds. The nature of the magnetic phase transition in

these compounds is weak first-order. Thus, the hysteresis losses hardly exist for the present samples, in comparison with 54.1 J/kg at 192 K (3 K higher than T_C) for its parent alloy $LaFe_{11.8}Si_{1.2}$. So, the compounds obtained are very suitable candidates for magnetic refrigerant near room temperature.

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$Ms(Tc^+) = 0$. Thus, there is a phase transition degree, such as defined by the value of $[Ms(Tc^-) - Ms(Tc^+)]/Ms(0)$, for a first order phase transition, namely, the character of a FOPT.

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