Effect of high pressure on the magnetocaloric property of $LaFe_{11.5}Si_{1.5}$

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(Received 4 January 2007; accepted 21 February 2007; published online 30 May 2007)

A field-induced magnetic entropy change under high pressure has been experimentally studied for the $LaFe_{11.5}Si_{1.5}$ compound. High pressure causes a linear decrease of the Curie temperature from ~194 to ~88 K, corresponding to a variation of the pressure from ~0 to 1 GPa. Appropriate pressures enhance the magnetic entropy change significantly in the meantime depressing the Curie temperature. A spike-shaped peak, followed by a plateau with a width of ~20 K, of the entropy change emerges and grows rapidly with the increase of pressure, and its maximum value is 138 J/kg K, obtained under the pressure of 1 GPa for a field change of 0–5 T. The pressure effect is also obvious on the entropy plateau. It results in an increase of the plateau height from ~23.8 J/kg K, without pressure, to ~29 J/kg K, when the pressure is 0.45 GPa. These results demonstrate the effectiveness of high pressure in modifying the entropy of $LaFe_{11.5}Si_{1.5}$. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2719004]

Magnetic refrigeration based on the magnetocaloric effect (MCE) of the materials is a promising technique because of its environmental protection and high energy efficiency. The discovery of $Gd_5Si_2Ge_2$,[1] $MnAs_{1-x}Sb_x$,[2] $MnFeP_{1-x}As_x$,[3] and $LaFe_{13-x}Si_x$[4,5] demonstrated the possibility to apply this technique near the ambient temperature and aroused a renewed interest in magnetic cooling.

A key issue for the MCE study is the control of phase transition, which is basically important to optimize the magnetocaloric property of the materials. It has been found that a first-order magnetic-crystallographic transformation could be induced by pressure, which modifies the MCE of the compound significantly.[6] A great enhancement MCE was also obtained in MnAs by applying an appropriate pressure.[7] The entropy change (ΔS) can be as high as ~267 J/kg K for a field change of 0–5 T when a constant pressure of 0.22 GPa exists. It is much larger than the theoretical value if only the magnetic entropy is accounted for. Based on a phenomenological model, Ranke *et al.*[8] presented an explanation to the giant MCE and believed that lattice entropy made a great contribution to ΔS.

Similar to MnAs, $LaFe_{13-x}Si_x$ ($1.2<x<1.8$) is an intermetallic showing a first-order magnetic transition accompanied by a large lattice expansion at the Curie temperature T_C. For this compound, a pressure-induced great change of magnetic coupling, demonstrated by the reduction of T_C at a rate of ~90 K/GPa, has been observed.[9] However, the spontaneous magnetization of the material remains essentially unaffected. These results suggest a possible modification of magnetic entropy change by pressure for this compound. Unlike MnAs, $LaFe_{13-x}Si_x$ exhibits a cubic structure, which guarantees the absence of structure transformation under high pressures. Therefore, the pressure effect is expected to be different for these two compounds.

In this article, we will report a systematic study of the pressure effect on the magnetocaloric property of $LaFe_{11.5}Si_{1.5}$. It is found that appropriate pressures enhance the magnetic entropy change significantly in the meantime depressing the Curie temperature. A spike-shaped peak, followed by a plateau with a width of ~20 K, of the entropy change emerges and grows rapidly with the increase of pressure, and its maximum value is 138 J/kg K, obtained under the pressure of 1 GPa for a field change of 0–5 T. The pressure effect is also obvious on the entropy plateau. It results in an increase of the plateau height from ~23.8 J/kg K, without pressure, to ~29 J/kg K, when the pressure is 0.45 GPa.

A polycrystalline compound with the nominal composition $LaFe_{11.5}Si_{1.5}$ was prepared by arc melting appropriate amounts of starting materials (99.9% in purity) under ultrapure argon atmosphere (~10 at. % excessive La was used to compensate the weight loss during the arc melting). The resultant ingot was annealed in an evacuated quartz tube at 1050 °C for one month, to improve the crystallization of the sample, and then quenched into liquid nitrogen. The phase purity and crystal structure of the sample was studied by x-ray diffraction. It is proved that the present sample crystallized in the $NaZn_{13}$-type cubic structure, and no secondary phases exist. The sample was set in a Teflon capsule filled with Fluorinert liquid pressure-medium (CF70:CF77=1:1) and compressed in a handmade miniature cell made of a

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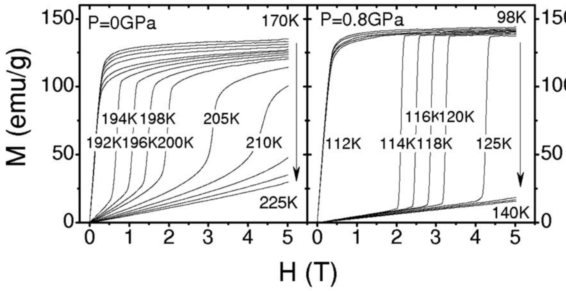

FIG. 1. Magnetization isotherms of $LaFe_{11.5}Si_{1.5}$ measured under the pressures of 0 and 0.8 GPa.

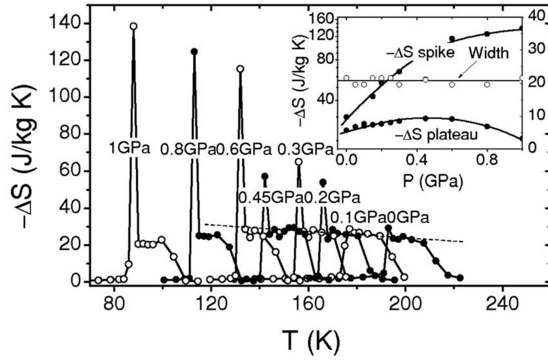

FIG. 2. Entropy changes as functions of temperature under various pressures, obtained for a field change of 0–5 T. Solid line shows the increase of entropy change with pressure. Inset plot displays the variation of the $-\Delta S$ spike, the $-\Delta S$ plateau, and its width with applied pressure.

Cu-Be alloy. The temperature and magnetic field dependences of magnetization under the hydrostatic pressures (P) up to 1 GPa were measured by using a quantum design superconducting quantum interference device magnetometer.

As expected, the Curie temperature exhibits a monotonic decrease with pressure. It reduces linearly from ~194 K for $P=0$ to ~88 K for $P=1$ GPa, as demonstrated by the thermal magnetization curves obtained under a field of 0.01 T (not shown). The rate for the T_C change is $d \ln T_C/dP \approx -0.713\ \mathrm{GPa}^{-1}$, considerably larger than that observed by Fujita *et al.* in $LaFe_{11.44}Si_{1.56}$ ($d \ln T_C/dP \approx -0.48\ \mathrm{GPa}^{-1}$).[9]

Figure 1 shows the typical magnetization isotherms, $M(H)$, of $LaFe_{11.5}Si_{1.5}$ obtained under the pressure of 0 and 0.8 GPa. Temperature steps of 2 K near T_C and 5 K far away from T_C were adopted for the measurement. In addition to the decrease of T_C, a remarkable observation is the sharpening of the itinerant-electron metamagnetic (IEM) transition under high pressures. When pressure is high, nearly all of the data collapse into two common curves that describe the $M-H$ dependence of the ferromagnetic and the paramagnetic states, respectively (right panel in Fig. 1), which demonstrates vividly the sudden switching, triggered by external fields, of the system between two definite states. Another distinctive feature is the increase of the threshold magnetic field (H_c) required for the IEM transition with pressure. As will be seen later, H_c is $\sim$0 without pressure and $\sim$1.9 T under the pressure of 0.8 GPa. The increase of H_c leads to a significant growth of the area enclosed by the $M-H$ curves at $T_c(H=0)$ and a vicinity temperature just above $T_c(H_c)$, which implies an apparent enhancement of the entropy change under pressure.

Magnetic entropy change can be calculated based on the Maxwell relation $\Delta S(T,H)=\int_0^H (\partial M/\partial T)_H dH$.[1,4] Figure 2 presents the $-\Delta S$ values as functions of temperature for a field change of 0–5 T under various pressures between $\sim$0 and 1 GPa. The $-\Delta S-T$ curve behaves as a flat plateau of the height of $\sim$24 J/kg K, depending on pressure and a width of $\sim$20 K for $P<0.1$ GPa. When the pressure exceeds 0.15 GPa, an extra spike-shaped peak much higher than the flat plateau appears. This peak remains and grows higher and higher with the increase of pressure and reaches a value of $\sim$138 J/kg K when $P=1$ GPa. Unlike the ΔS spike, the ΔS plateau first grows gradually with pressure, getting a maximum of $\sim$29 J/kg K at $P\approx 0.5$ GPa, then decreases considerably. Its maximum height is $\sim$20 J/kg K under the pressure of 1 GPa (inset in Fig. 2). Accompanying these behaviors, the ΔS peak moves gradually to low temperatures as observed in MnAs.[7]

The temperature span of the ΔS plateau is a consequence of the increase of the Curie temperature caused by external field. It would be interesting to check the variation of the ΔS width as the ΔS spike grows. Inset in Fig. 2 shows the pressure dependence of the $-\Delta S$ width, defined by the maximum temperature span of the $-\Delta S$ peak. The peak width is ~21 K and is essentially independent of pressure. This implies that the modification of the Curie temperature by magnetic field is generally not affected by high pressure.

There are two obvious differences between the pressure effects in MnAs and $LaFe_{11.5}Si_{1.5}$. First, the maximum ΔS spike appears under the pressure of $\sim$0.22 GPa in MnAs, and further increase in pressure causes a decrease of ΔS. The authors ascribed this behavior to structure transformation. In contrast, in $LaFe_{11.5}Si_{1.5}$, the ΔS spike shows a monotonic increase with pressure up to $P=1$ GPa, the maximum pressure for the present study. This implies the absence of pressure-triggered structure transition. Second, a rapid decrease both of the height and the width of the ΔS plateau with pressure was observed in MnAs and no ΔS plateau was visible in the case of $P>0.18$ GPa. An implicit inference from these results is that the appearance and growth of the ΔS spike occurs at the expense of the ΔS plateau. It is obviously not the case in $LaFe_{11.5}Si_{1.5}$ as demonstrated by Figs. 1 and 2.

There is a simple relation between the area of the ΔS peak and the saturation magnetization and applied field:[10] $\int_0^\infty \Delta S dT = -M_s \Delta H$, where S is the total entropy, M_s is the saturation magnetization, and ΔH is the field variation. A numerical calculation shows that this area increases linearly from ~558 J/kg for $P\approx 0$ to ~663 J/kg for $P=1$ GPa, well below the theoretical value ~850 J/kg ($M_s \approx 170$ emu/g has been adopted for $LaFe_{11.5}Si_{1.5}$). The discrepancy could be due to the integration of ΔS has been performed in a limited temperature range around T_C. This result indicates that the appearance of the ΔS spike does not violate the thermodynamic rule.

Based on the Clausius–Clapeyron equation $\Delta S = -\Delta M \Delta H/\Delta T_C$, the entropy change has a close relation with the variation of the Curie temperature caused by exter-

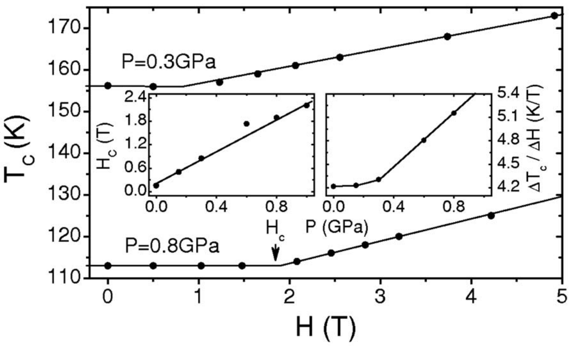

FIG. 3. Curie temperature as function of magnetic field obtained under two typical pressures of 0.3 and 0.8 GPa. Solid lines are guides for the eye. The inset plot shows the threshold field to drive the Curie temperature and the derivative of T_C with respect to H for $H > H_c$.

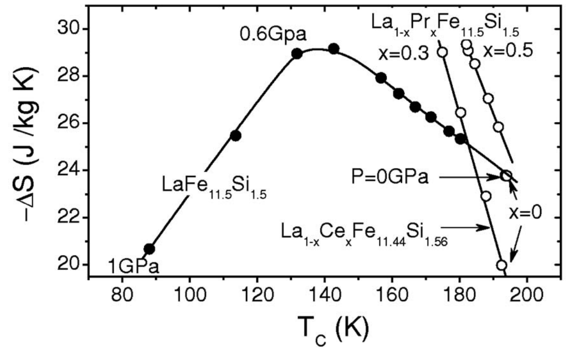

FIG. 4. Entropy change ($-\Delta S$ plateau) of $LaFe_{11.5}Si_{1.5}$ plotted against the Curie temperature that is tuned by pressure. The corresponding data of $La_{1-x}Ce_xFe_{11.44}Si_{1.56}$ (x=0, 0.1, 0.2, and 0.3) and $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ (x=0, 0.1, 0.2, 0.3, 0.4, and 0.5) are also shown for comparison. The data for the Ce doping are obtained under a field change of 0–2 T, others 0–5 T. Solid lines are guides for the eye.

nal field. To get a deep insight into the mechanism for the ΔS spike, it would be instructive to give a further analysis on the Curie temperatures under external fields and pressures. Figure 3 presents the variation of T_C with H and P. A remarkable observation is that under a high pressure the Curie temperature is nearly constant when magnetic field is low and increases with applied field following the relation $\Delta T_C \propto (H-H_c)$ after a threshold field H_c. This actually implies an extremely high ΔS near $T_C(H=0)$ considering the fact that ΔT_C is quite small below H_c. A further analysis reveals a nearly linear increase of H_c with P (inset in Fig. 3). It is nearly zero without pressure and ~1.9 T under a pressure of 0.8 GPa. This explains the monotonic increase of the ΔS spike with P. Our recent studies showed that similar behaviors appear in Pr-doped $LaFe_{13-x}Si_x$ (x=1.5). The experiments were performed with different temperature steps ranging from 0.5 to 2 K and essentially similar results were obtained (data not shown). These results confirm the occurrence of ΔS spike.

As a supplement, we would like to point out that the reasonability of the ultrahigh ΔS spike may require a further verification because of the presence of strong magnetic hysteresis in $LaFe_{13-x}Si_x$, which could hamper the applicability of the Clausius–Clapeyron equation.

In addition to the appearance of H_c, the $\Delta T_C-(H-H_c)$ slope varies with pressure (inset in Fig. 3). It is ~4.2 K/GPa without external pressure and ~5.1 K/GPa under a pressure of 0.8 GPa. The slope change is unobvious below ~0.3 GPa, and increases rapidly above 0.3 GPa. It is obvious that the enlarged ΔT_C will reduce the entropy change. Meanwhile, the magnetization jump at the field-induced phase transition increases gradually as the pressure drives T_C to low temperatures, which will cause an enhancement of entropy change. The complex variation of the ΔS plateau is actually a combined effect of these two factors.

Figure 4 is a comparison of the effects of pressure and Ce/Pr doping on the entropy change for the $LaFe_{13-x}Si_x$ compounds. The $-\Delta S$ plateau is 23.8 J/kg K for $P \approx 0$ and 29.2 J/kg K for P=0.45 GPa, the relative change is ~23%. An enhanced entropy change can also be obtained by doping Ce (Ref. 11) or Pr (Ref. 12) into the La sites and, fascinatingly, the maximum $-\Delta S$ has the similar values (~29.2 J/kg K for Ce doping and ~29.3 J/kg K for Pr doping) as that produced by high pressure. It is obvious that either applying a high pressure or doping smaller rare-earth atoms into the compounds will lead to a lattice contraction of $LaFe_{13-x}Si_x$. This will lead to a decrease of T_C, according to Bean and Rodbell[13] and, as a result, an enhancement of the first-order character of the phase transition of the compound. This is the apparent reason for the increase of the $-\Delta S$ plateau. Although the maximum entropy changes obtained by different techniques are nearly the same, the temperature where the maximum $-\Delta S$ plateau appears is considerably different. This suggests the difference of the mechanisms behind different processes, which requires further study.

This work has been supported by the National Natural Science Foundation of China, the National Basic Research of China, and the Grant-in-Aid for Scientific Research (No. 18540334) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

[1] V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).
[2] H. Wada and Y. Tanabe, Appl. Phys. Lett. **79**, 3302 (2001).
[3] O. Tegus, E. Brück, K. H. Buschow, and F. R. de Boer, Nature (London) **415**, 150 (2002).
[4] F. X. Hu, B. G. Shen, J. R. Sun, Z. H. Cheng, G. H. Rao, and X. X. Zhang, Appl. Phys. Lett. **78**, 3675 (2001).
[5] A. Fujita, S. Fujieda, Y. Hasegawa, and K. Fukamichi, Phys. Rev. B **67**, 104416 (2003).
[6] L. Morellon, Z. Arnold, C. Magen, C. Ritter, O. Prokhnenko, Y. Skorokhod, and P. A. Algarabel, Phys. Rev. Lett. **93**, 137201 (2004).
[7] S. Gama, A. A. Coelho, A. de Campos, A. M. G. Carvalho, and F. C. G. Gandra, Phys. Rev. Lett. **93**, 237202 (2004).
[8] P. J. von Ranke, A. A. S. G. Coelho, A. de Campos, A. M. G. Carvalho, F. C. G. Gandra, and N. A. de Oliveira, Phys. Rev. B **73**, 014415 (2006).
[9] A. Fujita, S. Fujieda, K. Fukamichi, H. Mitamura, and T. Goto, Phys. Rev. B **65**, 014410 (2001).
[10] A. M. Tishin and Y. I. Spichkin, *The Magnetocaloric Effect and Its Applications*, 1st ed. (Institute of Physics, Bristol, 2003), Vol. 1, Chap. 4, p. 418.
[11] A. Fujita, S. Fujieda, and K. Fukamichi, J. Appl. Phys. **99**, 08K910 (2006).
[12] J. Shen *et al.* (unpublished).
[13] C. P. Bean and D. S. Rodbell, Phys. Rev. **126**, 104 (1962).