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Properties of $NaZn_{13}$-type $LaFe_{13-x}Si_x$ (x=1.4, 1.5) compound with the first-order phase transition

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The investigations of dc magnetization, magnetic relaxation, specific heat, and electrical resistance for $LaFe_{13-x}Si_x$ (x = 1.4, 1.5) compounds have been carried out. Obvious thermal and magnetic hysteresis indicates that they experience a first-order phase transition. The phase transition temperature T'_C is driven to high temperature with the increasing of field, which can be described by the relation $T'_C(H)^2 - T'_C(0)^2 \propto H$. The large relaxation in magnetization around the field-induced metamagnetic transition field for $LaFe_{13-x}Si_x$ (x = 1.5) can be explained according to the thermal activation theory for the first-order phase transition and fitted by a logarithmic function $\frac{M(t)}{M_0} = 1 \pm Sln\left(\frac{t}{t_0} + 1\right)$, reflecting the distribution of energy barriers in this sample. The latent heat of $LaFe_{13-x}Si_x$ (x = 1.4) under zero field reaches to 1.8 kJ/kg. A good magnetic-thermal-resistive correspondence is also found in this compound. © *2012 American Institute of Physics*. [doi:10.1063/1.3671417]

Recently, much attention has been paid to the magnetic refrigeration based on the magnetocaloric effect (MCE) of solid-state working substances.[1–3] Giant MCE has been reported in materials with a magnetic first-order phase transition (FOPT), such as $Gd_5(Si, Ge)_4$,[1] $La(Fe, Si)_{13}$,[4,5] MnAs,[6,7] MnFe(P, As),[3] Ni_2MnGa,[8] etc. The origin of giant MCE is due to the stronger FOPT. This point can be easily understood by the Maxwell thermodynamic relation that predicts high entropy changes when the magnetization presents discontinuity at the critical temperature. For $LaFe_{13-x}Si_x$ compounds, the nature of phase transition changes from the second-order to the first-order with the increase of Fe concentration. Furthermore, the character of a FOPT is strengthened by further increasing the Fe content. In the work, we report systematically the properties of $LaFe_{13-x}Si_x$ (x = 1.4, 1.5) compounds with the first-order phase transition by analyzing the results of magnetization as functions of temperature, magnetic field and time, specific heat as a function of temperature, electrical resistance as functions of temperature and measurement times.

$LaFe_{13-x}Si_x$ (x = 1.4, 1.5) ingots were prepared by arc melting the starting materials with the purity better than 99.9 wt. % in high-purity argon atmosphere. The obtained ingots were turned over and remelted several times in order to ensure homogeneity. The as-cast bulk alloys were annealed in an evacuated sealed quartz tube at 1323 K for 50 days, and then quenched to room temperature or cooled to room temperature with the furnace. X-ray diffraction patterns at room temperature confirmed the single phase nature of the compounds, crystallizing in the cubic $NaZn_{13}$-type structure. Magnetic measurements were carried out by using a commercial MPMS-7 superconducting quantum interference device magnetometer and a commercial PPMS-14 H Physical Property Measurement System (Quantum Design). Heat capacity was also measured by using the latter measurement system. Electrical resistance measurements were done using a conventional four-probe method on heating, using the temperature and magnetic field conditions of the former measurement system.

Figures 1(a) and 1(b) show the zero-field cooling (ZFC) and field cooling (FC) temperature dependences of magnetizations (M) for $LaFe_{13-x}Si_x$ (x = 1.4, 1.5) compounds under different magnetic fields, respectively. In the ZFC mode, the sample was cooled to the first measuring temperature point before the measuring field (H) was switched on and the measurement was made while warming up the sample. The data were taken again in the presence of the same H when then cooling the sample. This was the FC mode. Before the measurement under the next field was performed, the previous applied field was switched off and the sample was warmed up to 300 K in order to eliminate the effect of magnetic history. Two compounds show the remarkable magnetization change with hysteresis around T'_C (corresponding to the maximum slope of M-T) for all of the magnetic fields studied because of the thermal-induced first-order transition. The correlation of magnetic coupling and a distortion of the lattice results in the appearance of the first-order transition.[9,10] Moreover, the thermal hysteresis reduces with the increase of magnetic field. The values of T'_C are 188 K and 196 K for $LaFe_{13-x}Si_x$ (x = 1.4, 1.5) under 0.1 T, respectively. For two compounds, T'_C shifts to high temperature with ascending magnetic field, as shown in the inset of Fig. 1(b). The variation of T'_C with field can be well fitted by the relation proposed by Shimizu to describe the FOPT,[11]

$$T'_C(H)^2 - T'_C(0)^2 \propto H, \tag{1}$$

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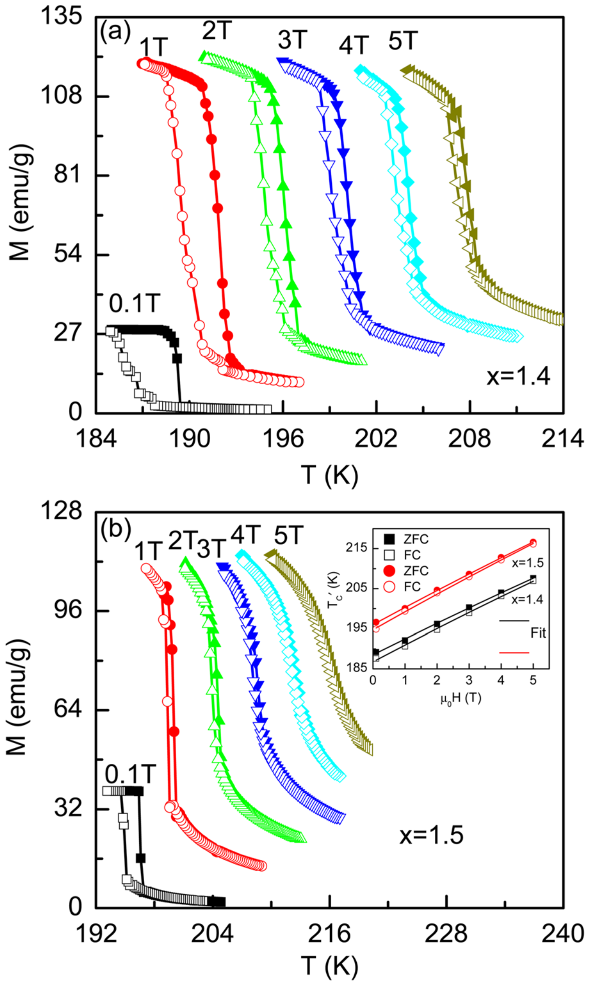

FIG. 1. (Color online) Temperature dependencies of ZFC (closed symbols) and FC (open symbols) magnetization for $LaFe_{11.6}Si_{1.4}$ (a) and $LaFe_{11.5}Si_{1.5}$ (b) under different magnetic field. The inset of (b) shows the field dependence of T_C' for $LaFe_{13-x}Si_x$ (x = 1.4, 1.5). The solid line is a fit based on Eq. (1).

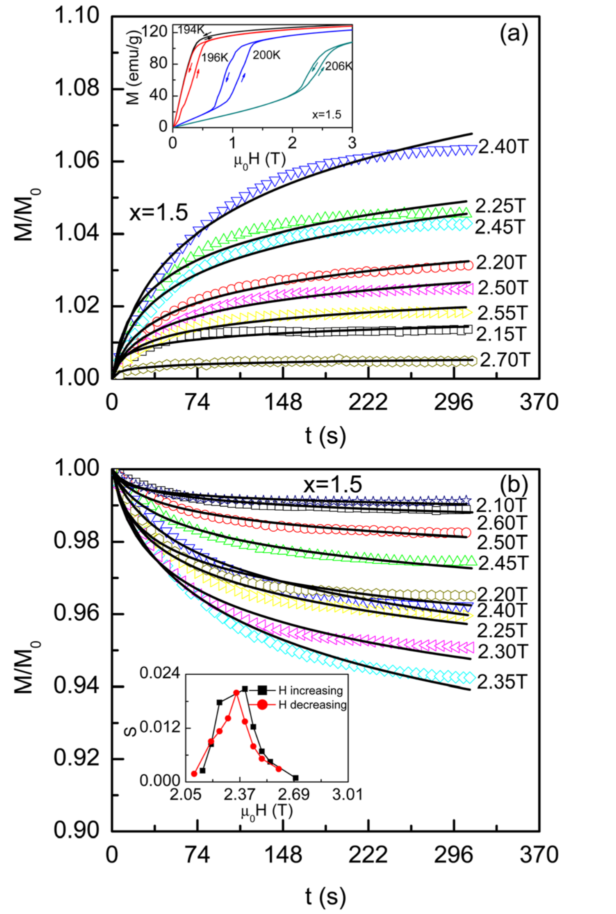

FIG. 2. (Color online) Normalized magnetization vs time curves for the compound measured at 206 K under typical fields during the increasing field (a) and decreasing field processes, the solid line is a fit based on Eq. (2). The inset of (a) shows the isothermal magnetization curves of $LaFe_{13-x}Si_x$ (x = 1.5) around phase transition temperature, where arrows indicate the sequence of measurements. The inset of (b) shows the variety of S with field.

where $T_C'(H)$ is the transition temperature under a certain magnetic field H, $T_C'(0)$ is the one under zero field.

The isothermal magnetization curves in the wide vicinity of phase transition temperature during the field ascending and descending processes ranging from 0 to 13 T for $LaFe_{13-x}Si_x$ (x = 1.5) have been measured. For the sake of clarity, the inset of Fig. 2(a) displays the data below 3 T around the phase transition temperature. Field-induced paramagnetic (PM)-ferromagnetic (FM) metamagnetic transition takes place above $T_C'(0)$. Meanwhile, obvious magnetic hysteresis can be found. The relaxation phenomenon in the range of metamagnetic transition field has been investigated. As an example, Figs. 2(a) and 2(b) present normalized M versus time (t) plots at $T = 206$ K ($\sim$10 K above $T_C'(0)$) under various H on the field increasing and decreasing paths, respectively. These $M(t)$ curves are well adjusted with a logarithmic function[12,13]

$$\frac{M(t)}{M_0} = 1 \pm Sln\left(\frac{t}{t_0} + 1\right), \tag{2}$$

where M_0 is the value of the magnetization recorded when the relaxation measurements were started, i.e., 0 s after the target T and H values were reached, "+" and "−" correspond to the field increasing and decreasing processes, respectively. The logarithmic rather than exponential dependence of M on t indicates that there is a distribution of energy barriers in the sample.[13,14] From Eq. (2) the magnetic viscosity S is extracted. The inset of Fig. 2(b) shows the variety of S with field. As the field increases in the magnetizing process, the thermal activation energy becomes large enough to allow the system to overcome the energy barriers and thermally activate the PM-to-FM transition. Consequently, the FM phase fraction shows a substantial growth as a function of time, and the magnetic relaxation rate increases. This explains the increase of S with increasing field. When the majority of the system becomes unblocked, a peak in $S(H)$ is observed at 2.4 T. S decreases gradually with further increasing field due to the weakening of magnetic relaxation. For the demagnetizing process, thermal activity energy induces that the FM-to-PM relaxation process occurs with the decrease of field. Therefore, the relaxation of magnetization reflects the thermally activated nucleation of the new phase. That is, the FM and PM phases nucleate in the magnetizing and demagnetizing processes, respectively.

One distinct character of a FOPT system is the existence of latent heat during the phase transition process. Here we focus on the $LaFe_{13-x}Si_x$ (x = 1.4) compound due to its stronger FOPT property. The heat capacity measurement of $LaFe_{13-x}Si_x$

(x = 1.4) was carried out by a relaxation method.[15] The temperature dependence of the specific heat C_P for $LaFe_{13-x}Si_x$ (x = 1.4) under zero field is given in Fig. 3. The specific heat exhibits a distinct peak and this temperature point agrees with T'_C under 0.1 T in Fig. 1(a). It is apparent that a clear λ-type peak of the specific heat is caused by the thermal-induced first-order transition. To obtain the value of C_P, the sample has been heated for 30 s and then been relaxed for 30 s. The inset of Fig. 3 displays the time dependence of temperature starting at 186.1 K. The heating power was given as 0.00145 W. As denoted by the arrow in the inset of Fig. 3, a flat plateau of temperature around 187.7 K is observed during the heating process, which originates in the existence of the latent heat in this FOPT system. From these data, we can estimate the value of latent heat for $LaFe_{13-x}Si_x$ (x = 1.4) under zero field, $\Delta Q/m = P\Delta t/m = 0.00145\ \mathrm{W} \times (14.01 - 10.97)\ \mathrm{s}/2.5\ \mathrm{mg} = 1.8\ \mathrm{kJ/kg}$.

The ZFC electrical resistance (R) curves of $LaFe_{13-x}Si_x$ (x = 1.4) have also been measured in the temperature range of 150–250 K under the successive fields of 0, 5, and 4 T (see Fig. 4). It is worth mentioning that these results are obtained based on the sample which were annealed and then cooled to room temperature with the furnace in order to depress the appearance of the tiny cracks. The resistance suddenly increases with increasing temperature, at which the FM-to-PM transition takes place. Moreover, the transition temperature of electrical resistance increases with the increasing of field. Namely, a good magnetic-resistive correspondence is observed. However, compared with the electrical resistance at the same temperature under the previous field, the value of electrical resistance under the current field ascends clearly. This is unreasonable and can be explained as following. For this compound, the magnetic phase transition accompanies with the large expansibility (constriction) of the lattice when the temperature is decreased (increased).[10] Each increasing-decreasing temperature cycle across the magnetic phase transition range results in the increase of tiny cracks, and then the increase of resistance. This opinion is further confirmed by the repetitious measurement result of resistance under the same field of 0 T (see the inset of Fig. 4(a)). The resistance changes abruptly around magnetic phase transition temperature for each measurement time. Furthermore, the resistances in the whole measurement temperature range increase greatly whenever the sample undergoes every cycle of increasing-decreasing temperature. These results also indicate that it is difficult to obtain the real variations of electrical resistance with temperature and magnetic field.

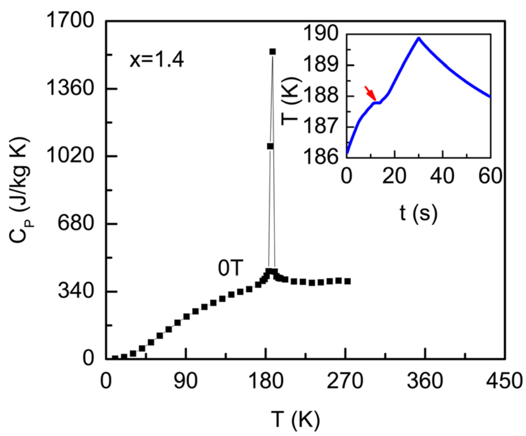

FIG. 3. (Color online) Temperature dependence of the specific heat C_P for $LaFe_{13-x}Si_x$ (x = 1.4) under zero field. Inset plot: temperature vs time curve for this compound starting at 186.1 K which is used to calculate the specific heat, the arrow indicates the flat plateau of temperature.

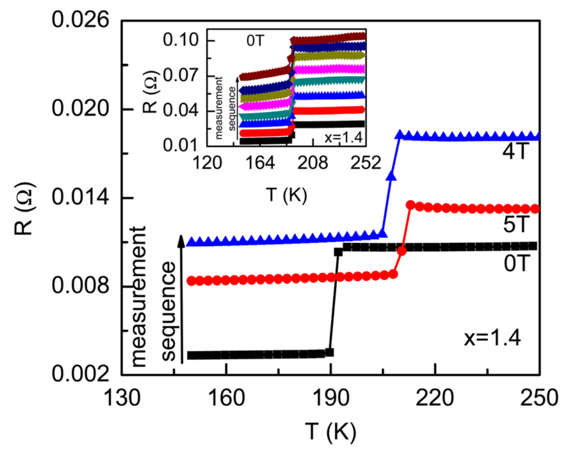

FIG. 4. (Color online) Temperature dependence of electrical resistance for $LaFe_{13-x}Si_x$ (x = 1.4) under fields of 0, 5, and 4 T. The inset displays the repetitious measurement curves of electrical resistance under zero field.

The results of isofield and isothermal magnetization curves illustrate that $LaFe_{13-x}Si_x$ (x = 1.4, 1.5) compounds undergo a first-order phase transition. The phase transition temperature is driven to high temperature with the increasing of field. The relationship between them can be well described by Eq. (1). The large magnetic relaxation in magnetization of $LaFe_{13-x}Si_x$ (x = 1.5) during the phase transitions reflects the distribution of energy barriers. The latent heat of $LaFe_{13-x}Si_x$ (x = 1.4) under zero field is obtained as 1.8 kJ/kg. Moreover, a good magnetic-thermal-resistive correspondence is observed in this compound.

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