Influence of the substitution of Cu for Si on magnetic entropy change and hysteresis loss in $LaFe_{11.7}(Si_{1-x}Cu_x)_{1.3}$ compounds

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The magnetic properties, magnetic entropy change, and hysteresis loss in $LaFe_{11.7}(Si_{1-x}Cu_x)_{1.3}$ compounds were investigated. It was found that the compounds retain the cubic $NaZn_{13}$ structure when the substitution of Cu reaches 20%. With increasing Cu content from $x=0$ to 0.2, the Curie temperature T_C increases from 185 to 200 K, while lattice parameter decreases from 11.475 to 11.468 due to the smaller atomic radius of Cu than Si. Metamagnetic behavior becomes weaker and magnetic entropy change $|\Delta S|$ drops with raising Cu content. However, $|\Delta S|$ still remains a large value, ~20 J/kg K, when x reaches 0.2. An attractive feature is that both thermal and magnetic hysteresis can be remarkably reduced by introducing Cu. The maximum hysteresis loss at T_C drops from 74.1 to 0 J /kg when the substitution of Cu for Si increases from 0% to 20%. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3063067]

Magnetic refrigeration based on magnetocaloric effect (MCE) has attracted much attention due to its superiority over the gas refrigeration on energy saving and environmental concerns.[1–3] Many materials with first-order magnetic phase transition have been discovered to exhibit great MCE.[1–7] The compounds $LaFe_{13-y}M_y$ (M=Al, Si) with cubic $NaZn_{13}$-type structure have been a focus of intensive studies because of their great MCE.[6–19]

For Si content in the range of $1.2 \leq y < 1.6$, phase transition in $LaFe_{1-y}Si_y$ is first order in nature, and a field-induced itinerant electron metamagnetic (IEM) transition takes place at temperatures just above T_C, which leads to a great MCE effect.[6–8] However, along with the appearance of the large MCE a concomitant hysteresis loss inevitably occurs because of the first-order nature of the phase transition. Therefore, improving the MCE of $LaFe_{1-y}Si_y$ with relatively low Si content is highly desired. Many efforts have been made on these materials. Replacement of Fe with Co has been attempted in $LaFe_{1-y}Si_y$ compounds, and a large MCE near room temperature has been observed.[9] It has also been found that partially replacing La with other rare-earth elements, such as Ce, Pr, and Nd, can greatly modify the MCE. A remarkable result is the depression of magnetic hysteresis by the incorporation of Pr.[10] However, up to now investigations on the substitution for Si were rarely reported. In this work, we report the influence of the substitution of Cu for Si on magnetic entropy change and hysteresis loss in $LaFe_{11.8}(Si_{1-x}Cu_x)_{1.2}$ compounds. It was found that magnetic properties, IEM behavior, and MCE effect are sensitive to Cu content. With increasing Cu content from $x=0$ to 0.2, T_C increases from 185 to 200 K. The magnetic entropy change drops but still remains a large value, ~20 J/kg K under 5 T, when the substitution of Cu for Si reaches 20%. More attractive is that raising Cu content can lead to a remarkable reduction in both thermal and magnetic hysteresis.

$LaFe_{11.7}(Si_{1-x}Cu_x)_{1.3}$ (x=0, 0.1, and 0.2) samples were prepared by arc-melting technique.[6] The obtained ingots were subsequently homogenized at 1373 K for 30 days, then quenched in liquid nitrogen. All magnetic measurements were performed using a superconducting quantum interference device magnetometer.

X-ray diffraction (XRD) analysis was carried out using Cu $K\alpha$ radiation to identify the crystal structure. Figure 1 shows the XRD pattern collected at room temperature. One can find that the samples are crystallized in a cubic $NaZn_{13}$-type structure even when the substitution of Cu for Si increases to 20%. A small amount of α-Fe impurity was detected in the presented samples (indicated by asterisk in Fig. 1), which is estimated to be 2–7 wt % based on the

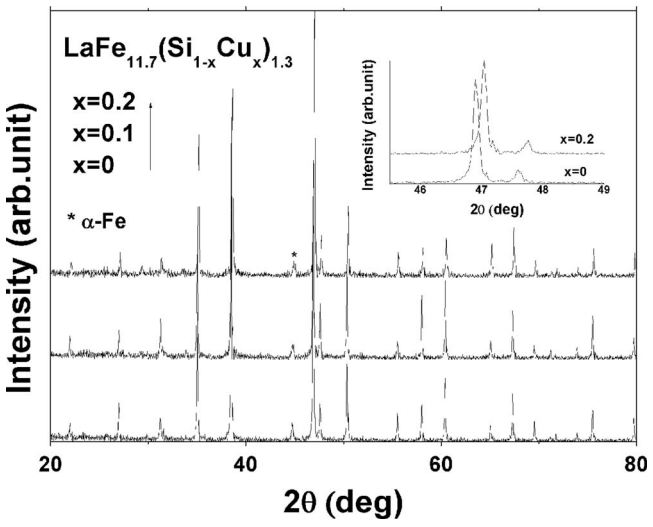

FIG. 1. XRD pattern collected at room temperature for $LaFe_{11.7}(Si_{1-x}Cu_x)_{1.3}$ compounds. The asterisk indicates the signal from α-Fe. Inset shows the details of XRD pattern around peak (531) for samples $x=0$ and 0.2.

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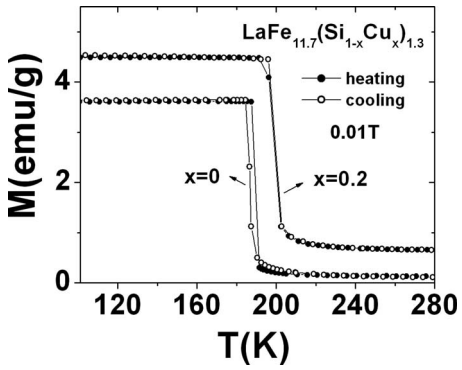

FIG. 2. Temperature dependent magnetization measured under 0.01 T on heating and cooling processes for samples $LaFe_{11.7}(Si_{1-x}Cu_x)_{1.3}$ ($x=0$, 0.2).

Rietveld refinement of XRD and EDX. Further increasing Cu would lead to appearance of a large amount of Fe impurities and inhomogeneity of the samples. Previous studies[11] indicated that the strong La–Si bonds play an important role in formatting the cubic $NaZn_{13}$ structure in $LaFe_{13-x}Si_x$ compounds. The mixing enthalpy is positive for La–Fe (+19 kJ/mol) but negative for La–Si (−58 kJ/mol). The replacement of La–Fe by La–Si pairs is the key factor that stabilizes the pseudobinary compound. However, redundantly introducing La–Si pairs, such as $LaFe_{13-y}M_y$ with $y>2.6$, will lead to the formation of a tetragonal structure instead of the cubic $NaZn_{13}$ structure.[20] The introduction of Cu may disturb the balance of La–Fe and La–Si pairs. If the ratio of the substitution of Cu for Si is high enough, the initial cubic structure can be destroyed, and a stable $NaZn_{13}$-type compound cannot be formed.

Inset of Fig. 1 shows the details of XRD pattern around the main peak (531) for the present samples. The notable shift of the peak to larger 2θ indicates that the lattice shrinks upon incorporating Cu, which can be attributed to the smaller radius of Cu than Si. The lattice parameter, obtained based on XRD pattern, reduces from 11.475 to 11.468 Å, but the Curie temperature T_C increases from 185 to 200 K as Cu increases from $x=0$ to $x=0.2$. Figure 2 displays the temperature dependent magnetization measured under 0.01 T in heating and cooling processes for samples $x=0$ and 0.2, respectively. T_C is defined as the maximum of dM/dT on cooling process. One can find that along with T_C increasing from 185 to 200 K, temperature hysteresis reduces. For the sample with $x=0$, a thermal hysteresis of 3 K is observed around T_C, indicating the presence of a thermal induced first-order magnetic transition. However, almost no thermal hysteresis is observed in the Cu-doped samples, implying that the incorporation of Cu weakens the first-order nature of the transition at T_C.

In $La(Fe,Si)_{13}$ systems with interstitial atoms, lattice expansion will lead to an increase in T_C because of the extension of Fe–Fe distance. However, an opposite behavior was observed in our samples with Cu incorporation. T_C increases with the reduction in lattice parameter. In pseudobinary $La(Fe,Si)_{13}$ systems, Fe atoms occupy two different sites Fe1 and Fe2, designed by the symbols 8b and 96i, respectively, and the Si and Fe atoms are randomly distributed at

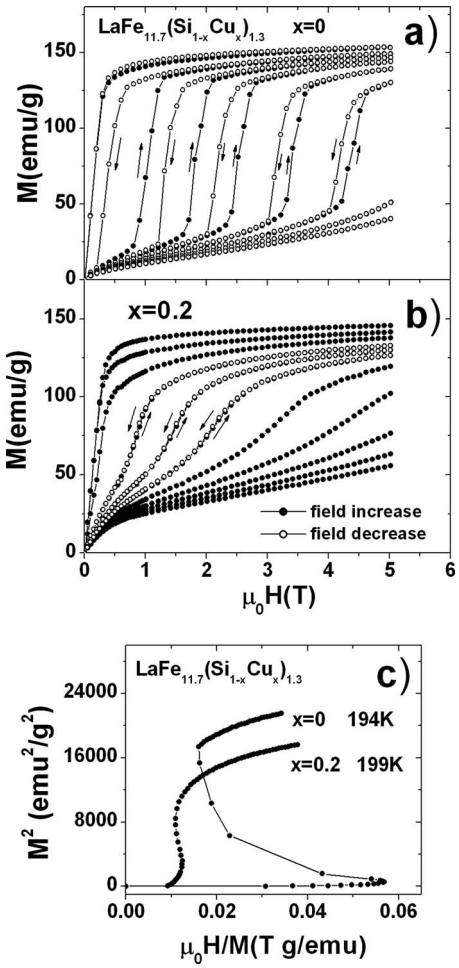

FIG. 3. Magnetization isotherms of $LaFe_{11.7}(Si_{1-x}Cu_x)_{1.3}$ measured on field increase and decrease. (a) $x=0$. (b) $x=0.2$. (c) Arrott plots for samples $x=0$ and 0.2.

96i sites. Previous studies[21,22] on Fe-based compounds indicated that Fe–Fe bond is a key factor that influences the magnetic properties and T_C. When the separation of the Fe–Fe pair is smaller than 2.45 Å, the Fe–Fe exchange interaction is negative, while a larger Fe–Fe distance will cause a positive interaction. Fe–Fe distance in $La(Fe,Si)_{13}$ has been demonstrated to be around the critical value. An expansion of unit lattice in $La(Fe,Si)_{13}$ with interstitial H or C atoms[12,13] causes a larger Fe–Fe distance, resulting in a stronger Fe–Fe exchange interaction, and then a shift of T_C to higher temperature. However, an opposite result was also observed in $LaFe_{13-y}Si_y$ with relative higher Si content, $1.6<y<2.6$, in which the lattice shrinks but T_C increases with increasing Si content. This phenomenon has been attributed to the increasing Fe1-Fe2 distance although the lattice constant decreases.[11] Similarly, the incorporation of Cu in the present samples may also affect the Fe–Fe bonds and thus magnetic properties and T_C. Detailed information of atomic site occupations, Fe–Fe bond length, and exchange interaction is required to fully understand the observed phenomena in present systems. Careful investigations are under way.

Shown in Fig. 3 are the typical magnetization isotherms (M-H) for $LaFe_{11.7}(Si_{1-x}Cu_x)_{1.3}$ ($x=0$, 0.2) measured in field increasing and decreasing processes. One can find that

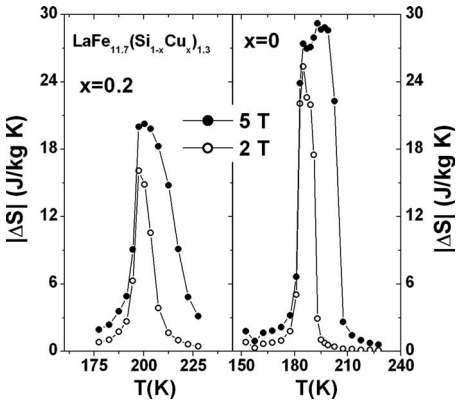

FIG. 4. Magnetic entropy change $|\Delta S|$ as functions of temperature and magnetic field for samples $LaFe_{11.7}(Si_{1-x}Cu_x)_{1.3}$ (x=0,0.2).

the M-H curves below T_C exhibit a characteristic ferromagnetic behavior for all samples. With increasing temperature above T_C, a field-induced IEM transition takes place, characterized by a sharp change in the magnetization. The observed nonlinear field dependence of magnetization at temperatures far above T_C is attributed to the α-Fe phase, which is consistent with the XRD analysis. For the Cu-free sample, a large magnetic hysteresis occurs. The maximum value of 74.1 J/kg appears at 190 K [see Fig. 3(a)]. When the substitution of Cu for Si reaches x=0.2, the magnetic hysteresis almost disappears at all temperatures [see Fig. 3(b)], indicating that the field-induced first-order transition from paramagnetic to ferromagnetic state was notably weakened upon introducing Cu. Figure 3(c) shows the compared Arrott plots for samples x=0 and 0.2. One can find that negative slopes still appear even for sample x=0.2, implying that a strong IEM behavior[23] retains although the hysteresis loss becomes almost 0. The strong IEM behavior without magnetic hysteresis predicts a large reversible MCE effect. The disappearance of hysteresis loss is very attractive for magnetic refrigeration technique.

Magnetic entropy change ΔS was calculated by using Maxwell relation based on the magnetization data.[1–3] Figure 4 shows the $|\Delta S|$ as functions of temperature and magnetic field for $LaFe_{11.7}(Si_{1-x}Cu_x)_{1.3}$ (x=0, 0.2) compounds. One can find that ΔS peak gradually broadens to higher temperature with increasing magnetic field, which is a result of the field-induced IEM transition from paramagnetic to ferromagnetic state at temperatures above T_C.[6] The maximum $|\Delta S|$ under 2 and 5 T magnetic fields are found to be 25.0 and 29.1 J /kg K for samples x=0, 16.1, and 20.2 J/kg K for x=0.2, respectively. As a result of the increase in T_C, the $|\Delta S|$ peak shifts toward higher temperatures. Although $|\Delta S|$ exhibits a reduction in value, the maximum $|\Delta S|$ in $LaFe_{11.7}Si_{1.04}Cu_{0.26}$ still attains 20.2 J/kg K for a field change of 0–5 T, which comes from the strong IEM behavior. More important is that no magnetic hysteresis loss appears in this sample, indicating a completely reversible MCE.

In conclusion, the influence of the substitution of Cu for Si on magnetic entropy change and hysteresis loss was investigated in $LaFe_{11.7}(Si_{1-x}Cu_x)_{1.3}$. The compounds retain the cubic $NaZn_{13}$ structure when the substitution is within 20%. The incorporation of Cu causes an increase in T_C. Although the compounds exhibit a reduced $|\Delta S|$ value, the maximum $|\Delta S|$ still attains 20.2 J/kg K under 5 T when the Cu content is increased to x=0.2. The first-order nature of phase transition becomes weak, resulting in a remarkable reduction in both thermal and magnetic hysteresis. The maximum hysteresis loss drops from 74.1 to 0 J/kg for $LaFe_{11.7}(Si_{1-x}Cu_x)_{1.3}$ with x varying from 0 to 0.2.

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