Magnetocaloric effect in itinerant electron metamagnetic systems $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$

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The $NaZn_{13}$-type compounds $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ ($x=0.04$, 0.06, 0.08) were successfully synthesized, in which the Si content is the limit that can be reached by arc-melting technique. T_C is tunable from 243 to 301 K with Co doping from $x=0.04$ to 0.08. Great magnetic entropy change ΔS in a wide temperature range from ~230 to ~320 K has been observed. The adiabatic temperature change ΔT_{ad} upon changing magnetic field was also directly measured. ΔT_{ad} of sample $x=0.06$ reaches ~2.4 K upon a field change from 0 to 1.1 T. The temperature hysteresis upon phase transition is small, ~1 K, for all samples. The influence of Co doping on itinerant electron metamagnetic transition and magnetic entropy change is discussed. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1847071]

Magnetocaloric effect (MCE) has been a topic of intense research in the past decades. MCE is induced via the coupling of the magnetic sublattice with the magnetic field. It can be characterized by isothermal entropy change ΔS, as well as adiabatic temperature change ΔT_{ad}. The compounds with cubic $NaZn_{13}$-type structure have been recently suggested to be appropriate materials for exploring efficient magnetic refrigerants.[1–4] The large magnetic entropy change reported in this class of ferromagnetic materials warrants further experimental and theoretical studies. The $NaZn_{13}$-type compounds $LaFe_{13-x}Si_x$ with low Si content show an itinerant electron metamagnetic transition above Curie temperature T_C and a negative lattice expansion at T_C. With decreasing Si content, the nature of the phase transition evolves from second-order to first-order and the first-order nature is strengthened by further reducing the Si content. We found that incorporation of Co weakens the first-order nature of the transition and drives T_C to a higher temperature. A proper combination of Si and Co could make T_C near room temperature and preserve the first-order nature of the transition, which is characterized by a sharp change of lattice parameter. In this paper, we successfully synthesized $NaZn_{13}$-type compounds $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ ($x=0.04$, 0.06, 0.08), in which the Si content is the lowest limit that can be reached by arc-melting technique, and systematically investigated their magnetocaloric effect. T_C is tunable from 243 to 301 K with Co doping from $x=0.04$ to 0.08. The influence of Co doping on itinerant electron metamagnetic transition and magnetic entropy change is discussed.

The samples employed in the present investigation were prepared by repeated arc-melting appropriate amounts of starting materials. The commercial purity of the starting materials La, Fe, Co, and Si are 99.9 wt %, 99.99 wt %, 99.9 wt %, and 99.999 wt %, respectively. The ingots were wrapped with Ta foil individually and homogenized in a sealed quartz tube with a high vacuum of 10^{-4} Pa for 30 days at 1323 K, then quenched in liquid nitrogen. Quenching is important to obtain a stable compound with low Si content for this class of alloys. The Si composition in present samples $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ ($x=0.04$, 0.06, 0.08) is the limit that can be reached by using such a synthesizing method. Further reducing Si content would cause appearance of a large amount of α-Fe. X-ray diffraction (XRD) analysis show that the present samples crystallized in a single phase of cubic NaZn13-type structure. A minor α-Fe impurity was observed, the amount of which is around 4–6 wt % estimated from Rietveld refinement of the XRD data, as well as the chemical analysis by inductively coupled plasma-atomic emission spectrometry (ICP-AES). All magnetic measurements were performed using a superconducting quantum interference device (SQUID) magnetometer. The Curie temperature T_C was determined to be 243, 274, and 301 K for samples $x=0.04$, 0.06, 0.08 from the temperature dependent

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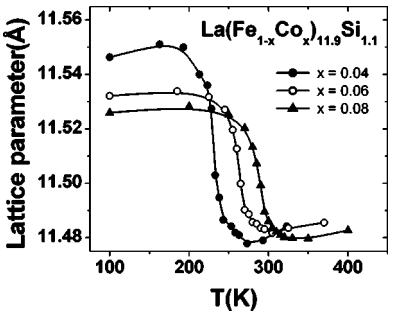

FIG. 1. The temperature dependent lattice parameter of $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ ($x=0.04$, 0.06, 0.08) compounds.

magnetization measured under a field of 0.01 T. The direct measurement of magnetocaloric effect was carried out under adiabatic conditions with a continuous registration of a temperature change upon a fast increase of applied magnetic field. The rate of the field change is about 0.7 T/s. The accuracy of the measurements is about 5%.

In order to study the structure change on altering magnetic state with temperature, XRD measurements at various temperatures were performed for all samples. It is found that the crystal structure remains cubic $NaZn_{13}$-type, but the lattice parameter changes dramatically at T_C, implying a first-order transition. Figure 1 shows the temperature dependence of lattice parameter obtained from the XRD spectra, noting the large negative thermal expansion near T_C. The lattice parameter in the ferromagnetic state, for different samples $x=0.04$, 0.06, and 0.08, is bigger than that in the paramagnetic state by ~0.63%, 0.44%, and 0.41%, respectively, in the vicinity of T_C. The substitution of Co for Fe atoms influences the magnetovolume effect. The amount of lattice contraction gradually decreases with increasing Co doping. Careful measurements of ac susceptibility on heating and cooling indicate that temperature hystereses of the transitions for all samples are small, ~1 K. In the past, several theories were used to describe magneto-elastic effect in itinerant magnetic systems.[5,6] A widely used theory is the local-moment volume magnetostriction, in which the magnetovolume effect arises from the volume dependence of the exchange integral between spins. A theory developed by applying the Stoner band model suggested that the magnetovolume effect is connected with the increase of the kinetic energy of the electron system due to the splitting of the 3*d* band. For LaFeAl compounds with $NaZn_{13}$-type structure, previous investigations[5] indicated that the magnetovolume effect comes from both the local-moment and band part, but the latter contributes much more than the former. For understanding the origin of the large negative expansion near T_C in present compounds, detailed information about the band structure is still needed.

Figure 2(a) displays the magnetization isotherms of $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ ($x=0.04$, 0.06, 0.08) measured on field increase in a wide temperature range with different temperature steps. In the vicinity of T_C, the temperature step of 2 K is chosen and a step of 5 K for the far regions. Figure 2(b) shows selected *M–H* curves for increasing and decreasing fields. One can find that the magnetic hysteresis upon altering field is small for all samples. Moreover, the substitution

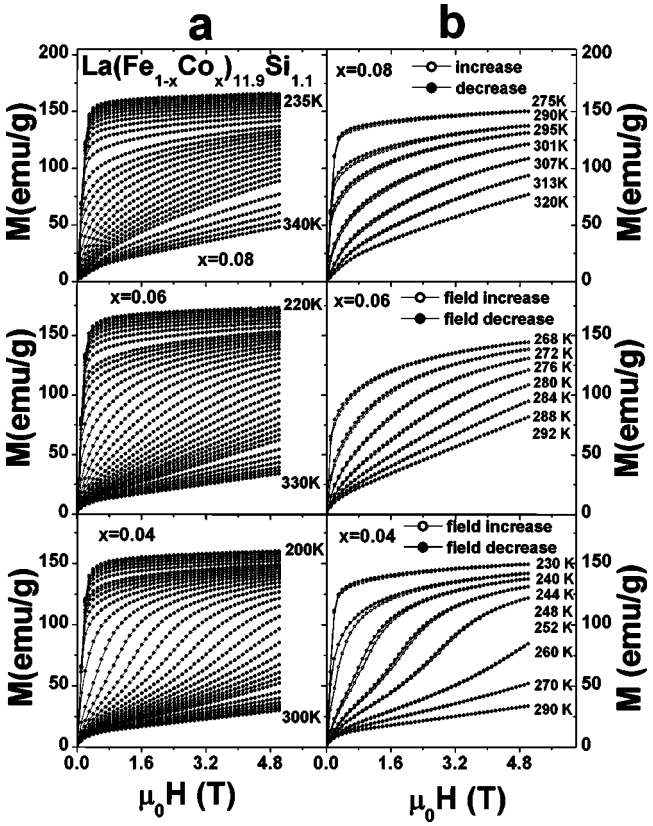

FIG. 2. Magnetization isotherms of $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ ($x=0.04$, 0.06, 0.08) compounds. (a) Isotherms on field increase. Temperature step is 2 K in the vicinity of T_C, and 5 K for the regions far away from T_C. (b) Selected isotherms measured on field increase and decrease.

of Co for Fe atoms further reduces the magnetic hysteresis. The small field hysteresis is considered to be a favorable characteristic for magnetic refrigeration applications.

Figure 3 shows the magnetic entropy change ΔS as functions of temperature and magnetic field obtained by using Maxwell relation $\Delta S(T,H)=\int_0^H(\partial M/\partial T)_H dH$.[1–4] The ΔS of Gd is also presented for comparison. One can find that the $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ compounds show large ΔS in a wide temperature range from ~230 to ~320 K. The ΔS significantly exceeds that of Gd. The ΔS magnitude decreases with increasing Co doping, which may correlate with the weakness of the magnetovolume effect (see Fig. 1). The weaken-

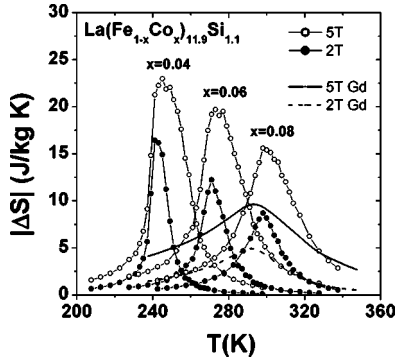

FIG. 3. Magnetic entropy change $|\Delta S|$ of $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ ($x=0.04$, 0.06, 0.08) in comparison with that of Gd for the magnetic field changes from 0 to 2 and from 0 to 5 T.

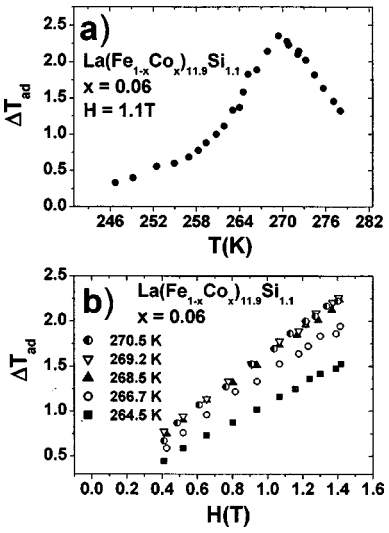

FIG. 4. (a) Adiabatic temperature change ΔT_{ad} of sample $x=0.06$ as a function of temperature obtained by direct measurements upon a field change from 0 to 1.1 T. (b) The ΔT_{ad} as a function of applied magnetic field for different temperatures.

ing of magnetovolume effect would lead to a lessening of the slope of M–T curves near T_C, and thus a decrease of ΔS according to Maxwell relation.

The asymmetrical broadening of ΔS peak with increasing field for $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ is also observed, which is a result of the field-induced itinerant-electron metamagnetic (IEM) transition from paramagnetic to ferromagnetic state above T_C.[1] Increasing Co content makes the phenomenon of asymmetrical broadening become weak. It seems that the substitution of the Co for Fe atoms can suppress the IEM transition in the present compounds. The phenomenon of IEM transition was historically observed in many *d* electron systems. Yamada discussed it by taking into account the effect of spin fluctuations on the Ginzburg–Landau theory.[7] The field-induced IEM transition is closely associated with the double minima of the paramagnetic and the ferromagnetic state in the magnetic-free energy as a function of magnetization. The applied fields drive the energy minimum of ferromagnetic state lower than that of paramagnetic state above T_C, resulting in the IEM transition. Generally, IEM transition is related to a special *d* electron band structure which exhibits a sharp peak of the density of states (DOS) just below the Fermi level.[7] It is known that the IEM transition in Laves phase compounds are attributed to unique Co 3*d* band structure.[7,8] Unfortunately, no information on the band structure is available for present compounds. Their IEM transition may be influenced by not only the electronic structure but also the elastic energy change.[7–9] A reduction of the elastic energy change with Co doping (see Fig. 1) may be a possible reason of the gradual weakness of the IEM transition with increasing Co content.

In order to make sure the potential of present compounds as candidates for magnetic refrigerants, we chose sample $x=0.06$ and directly measured the adiabatic temperature change ΔT_{ad} upon a change of magnetic field. Figure 4(a) displays the temperature dependent ΔT_{ad} collected on heating the sample from 240 K to 280 K upon a field change from 0 to 1.1 T. One can see the peak value of ΔT_{ad} reaches 2.4 K. The peak position of ΔT_{ad} was found around 3 K less than T_C defined by thermal magnetization curves. This difference in picking ΔT_{ad} temperature and T_C may be explained by a simple thermodynamic model[10] and could be accounted as quite reasonable. The field dependent ΔT_{ad} collected at different temperatures in the vicinity of T_C is shown in Fig. 4(b). One can find that ΔT_{ad} collected at present temperatures starts to increase at the same magnetic field of $H \sim 0.4$ T, and has a nearly linear dependence on applied field in the region of $0.4\ \mathrm{T} < H < 1.4$ T. All ΔT_{ad} curves do not display a saturation behavior. It means that adiabatic temperature change would increase noticeably with increasing field.

In summary, $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ ($x=0.04$, 0.06, 0.08) compounds with tunable T_C from 243 to 301 K are successfully synthesized, in which the Si content reaches the lowest limit by using the present synthesis method. The magnetic ordering at T_C is accompanied by a large increase of lattice parameter without changing the $NaZn_{13}$-type structure. The transition is of first-order in nature with small temperature and field hystereses. Large magnetic entropy change in a wide temperature range from ~230 to ~320 K is observed. The substitution of Co for Fe increases T_C but reduces the amount of lattice contraction and suppresses the IEM transition gradually, thereby leads to a decrease of ΔS and weakens the asymmetrical broadening of the ΔS peak. The results of adiabatic temperature change obtained by direct measurements are also reported. Large values of the isothermal entropy change and adiabatic temperature change together with nonsaturated behavior of the field dependence of the MCE confirmed the large potential of present compounds as magnetic refrigerants in a wide temperature range near room temperature.

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