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Effect of Co substitution on magnetic properties and magnetic entropy changes in $LaFe_{11.83}Si_{0.94}Al_{0.23}$ compounds*

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Effect of Co substitution on magnetic properties and magnetic entropy changes in $LaFe_{11.83}Si_{0.94}Al_{0.23}$ compounds has been investigated by means of magnetization measurements. X-ray diffraction shows the prepared compounds to be single phase with the cubic $NaZn_{13}$-type structure. Substitution of Co for Fe leads to an increase of Curie temperature of the material. The magnetic entropy changes in $LaFe_{11.83}Si_{0.94}Al_{0.23}$ and $LaFe_{11.03}Co_{0.80}Si_{0.94}Al_{0.23}$ compounds are 21.8J/(kg·K) to 16.9J/(kg·K) under a magnetic field change of 0–5T at Curie temperature, respectively. Giant magnetic entropy changes are attributed to the higher magnetization and the rapid change in magnetization at Curie temperature.

Keywords: $LaFe_{11.03}Co_{0.80}Si_{0.94}Al_{0.23}$ compounds, magnetic property, magnetic entropy change
PACC: 7530S

1. Introduction

In recent years, a number of investigations have been made on the room-temperature magnetic refrigerant in view of its wide practical application with high efficiency and environmental cleanliness in comparison with conventional gas refrigeration. Many ferromagnetic materials with second-order magnetic transition have been systematically studied in an attempt to achieve a large magnetocaloric effect (MCE). Gd was considered historically to be the only useful material as a room-temperature magnetic refrigerant owing to its magnetic entropy change ΔS near room temperature (ΔS ~9.8J/(kg·K) under a magnetic field change of 0–5T at Curie temperature T_C=293K).[1] Recently, in order to get larger MCE, much attention has been paid to materials with a first-order transition [2−9] because a first-order transition tends to concentrate $|\Delta S|$ to a narrow temperature range around the transition temperature compared with a second-order one, which implies that large $|\Delta S|$ is much easier to obtain in the vicinity of transition temperature. Indeed, large magnetic entropy change has been observed in rare-earth rich or 3d-transition-metal rich systems with a first-order magnetic transition, such as $Gd_5Si_2Ge_2$,[2,3] La(Fe, Si)$_{13}$,[4,10] $MnFeP_{0.45}As_{0.55}$[11] and $MnAs_{1-x}Sb_x$.[5] It is found that with decreasing Si content in La(Fe, Si)$_{13}$ the nature of the phase transition at T_C changes from second-order to first-order and the first-order nature is strengthened by further reducing the Si content, at the same time lowering T_C. Recent research has also confirmed that the addition of small amount of Co and the introduction of interstitial atoms leads to an increase of Curie temperature, without losing the large magnetic entropy change.[6,7,10] In this paper, we report the effect of substitution of Co for Fe on the magnetic properties and magnetic entropy changes in La(Fe, Si)$_{13}$ compounds with Al substitution.

2. Experiment

$LaFe_{11.83}Si_{0.94}Al_{0.23}$ and $LaFe_{11.03}Co_{0.80}Si_{0.94}Al_{0.23}$

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compounds were prepared by arc melting the constituent metals in an atmosphere of high purity argon. The raw materials of La, Fe, Co, Si and Al were at least 99.9% pure. An excess 10at% of La is added to compensate for the loss during melting. The ingots were remelted three times to ensure homogeneity. The arc-melted ingots were wrapped in Ta foil, sealed in an evacuated quartz tube and then annealed at 1307K for 2 months, followed by quenching quickly into the liquid nitrogen. Powder x-ray diffraction (XRD) with Cu Kα radiation was used to identify the phase structure and to determine the crystal structure and lattice parameters. Curie temperature was determined from the temperature dependence of the magnetization measured with a superconducting quantum interference device (SQUID) magnetometer in a field of 0.01T. The magnetic entropy change was calculated from the isothermal magnetization at temperatures near T_C measured with a SQUID magnetometer under a magnetic field change of 0–5T.

3. Results and discussion

The room temperature powder XRD patterns of $LaFe_{11.83}Si_{0.94}Al_{0.23}$ and $LaFe_{11.03}$ $Co_{0.80}Si_{0.94}Al_{0.23}$ compounds are shown in Fig.1: the present compounds crystallize in the cubic $NaZn_{13}$-type structure (Fm3c). A minor phase α-Fe was also observed in the $LaFe_{11.83}Si_{0.94}Al_{0.23}$ sample. The room-temperature lattice parameter a is 1.1492 and 1.1505nm for the two samples, respectively.

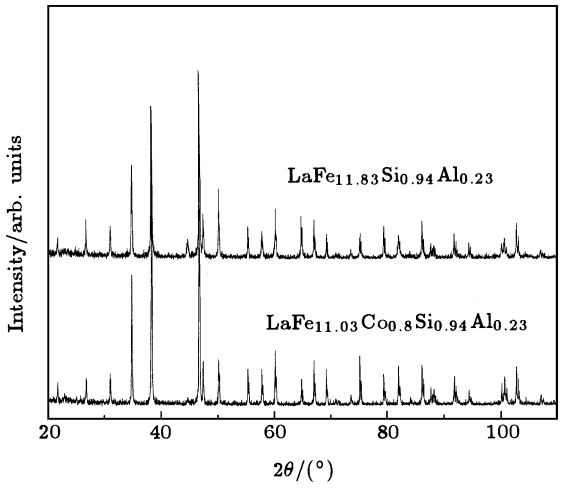


Fig.1. XRD pattern for $LaFe_{11.83}Si_{0.94}Al_{0.23}$ and $LaFe_{11.03}Co_{0.80}Si_{0.94}Al_{0.23}$ compounds.

Figure 2 shows the temperature dependence of the magnetization for $LaFe_{11.83}Si_{0.94}Al_{0.23}$ and $LaFe_{11.03}Co_{0.80}Si_{0.94}Al_{0.23}$ compounds measured under an applied magnetic field of 0.01T. Curie temperatures T_C, determined as the temperature corresponding to the minimum of dM/dT, is 176 and 282K for $LaFe_{11.83}Si_{0.94}Al_{0.23}$ and $LaFe_{11.03}Co_{0.80}Si_{0.94}Al_{0.23}$ compounds, respectively. One can see that T_C increases significantly with substitution of Co for Fe. In $LaFe_{11.83}Si_{0.94}Al_{0.23}$ and $LaFe_{11.03}Co_{0.80}Si_{0.94}Al_{0.23}$ compounds, La is nonmagnetic and the Curie temperature is mainly determined by the magnitude of the exchange interactions between transition atoms. For the Co-substituted compound, the Curie temperature is determined by the Fe–Fe, the Fe–Co and the Co–Co interactions. The increase of Curie temperature in the Co-substituted compound is probably associated with the fact that the interaction between Co moments in metal systems is always ferromagnetic, and the Fe–Co and the Co–Co interactions are much larger than the Fe–Fe ones. Therefore, the substitution of Co for Fe in the $LaFe_{11.83}Si_{0.94}Al_{0.23}$ results in the increase of Curie temperature, as observed in previous reports on the Fe–Co based compounds.[12]

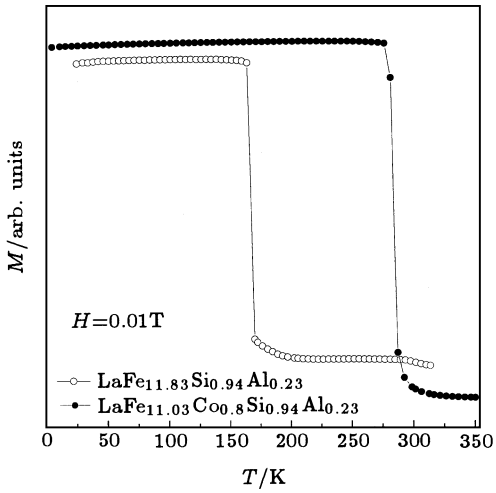


Fig.2. Temperature dependence of the magnetization of $LaFe_{11.83}Si_{0.94}Al_{0.23}$ and $LaFe_{11.03}Co_{0.80}Si_{0.94}Al_{0.23}$ compounds measured under a low magnetic field of 0.01T.

The thermal magnetization curves measured in an applied magnetic field of 1T are shown in Fig.3 for $LaFe_{11.83}Si_{0.94}Al_{0.23}$ and $LaFe_{11.03}Co_{0.80}Si_{0.94}Al_{0.23}$ compounds, together with that of Gd for comparison. The change in magnetization in the present compounds at Curie temperature is much larger than that of Gd. The almost discontinuous change of magnetization with temperature around T_C suggests that a first-order magnetic transition occurs in the samples. From the magnetization curve at 5K, the saturation magnetization for $LaFe_{11.83}Si_{0.94}Al_{0.23}$

and $LaFe_{11.03}Co_{0.80}Si_{0.94}Al_{0.23}$ compounds was determined to be 161.5 and 162.3 emu/g, respectively. The high magnetization and the rapid change in magnetization associated with the first-order magnetic transition result in a large magnetic entropy change. Figure 3 shows magnetization measured with increasing (full symbols) and decreasing (open symbols) temperature for $LaFe_{11.03}Co_{0.80}Si_{0.94}Al_{0.23}$ compound. The thermal hysteresis has the nature of a first-order phase transition. The small size of the temperature hysteresis indicates that the magnetization process can be considered as being reversible in temperature, as shown in previous reports on $MnFeP_{0.45}As_{0.55}$[11] and La–Fe–Co–Si compounds.[4]

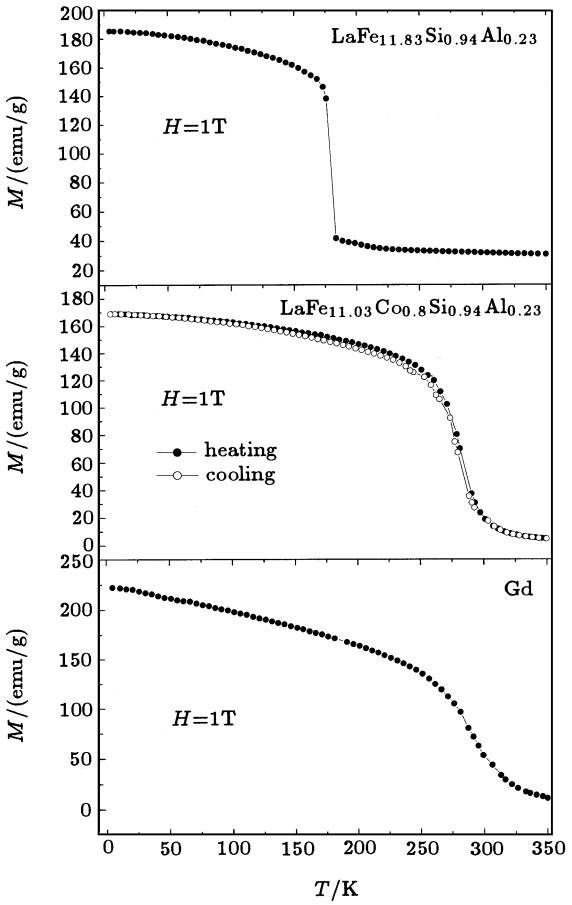


Fig.3. Thermal magnetization curves measured in an applied magnetic field of 1T for $LaFe_{11.83}Si_{0.94}Al_{0.23}$ and $LaFe_{11.03}Co_{0.80}Si_{0.94}Al_{0.23}$ compounds and Gd.

Figures 4(a) and (b) show the magnetization isotherms of $LaFe_{11.83}Si_{0.94}Al_{0.23}$ and $LaFe_{11.03}Co_{0.80}Si_{0.94}Al_{0.23}$ compounds measured in an increasing field in a wide temperature range with different temperature steps, respectively. In the vicinity of Curie temperature, from 165 to 195K, a step of 2K is chosen, and a step of 5K is chosen for the far regions of 125–165K and 195–225K, for $LaFe_{11.83}Si_{0.94}Al_{0.23}$,

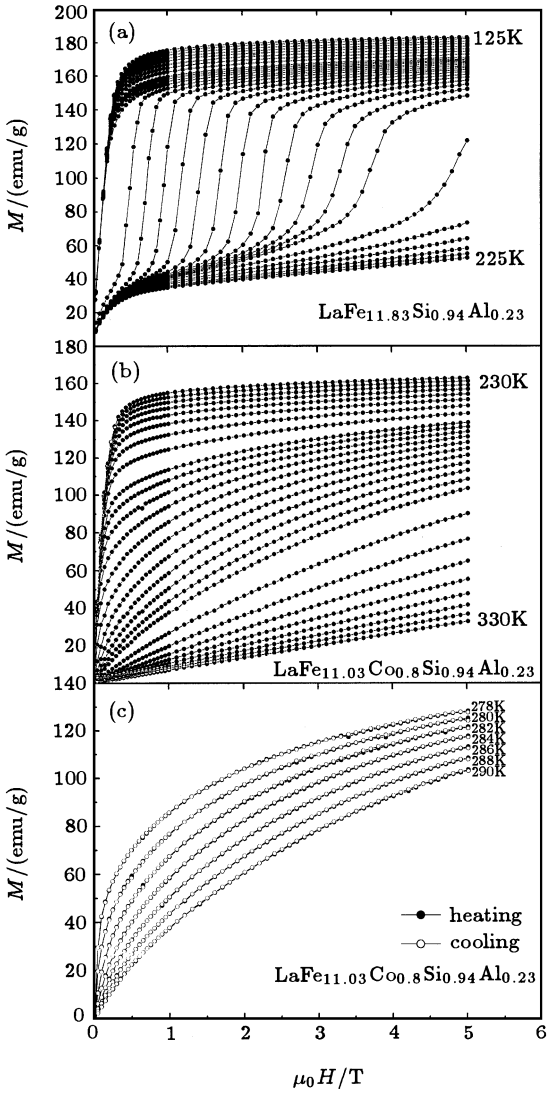


Fig.4. Magnetization isotherms of $LaFe_{11.83}Si_{0.94}Al_{0.23}$ (a) and $LaFe_{11.03}Co_{0.80}Si_{0.94}Al_{0.23}$ (b) compounds, the temperature step is 2K in the vicinity of T_C, and 5K for the regions far from T_C; (c) Magnetization isotherm of $LaFe_{11.03}Co_{0.80}Si_{0.94}Al_{0.23}$ compound with increasing and decreasing field in the vicinity of T_C.

and the in regions of 270–290K a step of 2K and in the regions of 230–270K and 290–330K a step of 5K are chosen for $LaFe_{11.03}Co_{0.80}Si_{0.94}Al_{0.23}$ compounds. The sweep rate of the field is slow enough to ensure that the M–H curves are recorded in an isothermal mode. It is evident from Fig.4(c) that every isotherm for $LaFe_{11.03}Co_{0.80}Si_{0.94}Al_{0.23}$ compound shows a reversible behaviour upon the field increase and decrease. One knows that a completely reversible MCE requires that there is no hysteresis in the magnetization as a function of both the temperature and the magnetic field. A small magnetic hysteresis during increasing and decreasing of field for $LaFe_{11.83}Si_{0.94}Al_{0.23}$ and $LaFe_{11.03}Co_{0.80}Si_{0.94}Al_{0.23}$

compounds can be considered as a very favourable characteristic for magnetic refrigerant applications.

The magnetic entropy change $|\Delta S|$ is calculated from magnetization data by means of the equation [2,3,5,11,13]

$$\Delta S(T,H) = \int_0^H (\partial M/\partial T)_H \mathrm{d}H,$$

which is based on the Maxwell relation. Figure 5 shows the temperature dependence of $|\Delta S|$ of $LaFe_{11.83}Si_{0.94}Al_{0.23}$ and $LaFe_{11.03}Co_{0.80}Si_{0.94}Al_{0.23}$ compounds under different magnetic field changes. The calculated maximum values $|\Delta S|_{\mathrm{m}}$ of magnetic entropy changes are 20.1 and 9.1J/(kg·K) for field change from 0 to 2T, and 21.8 and 16.9J/(kg·K) for field change from 0 to 5T, respectively. It is evident that the $|\Delta S|_{\mathrm{m}}$ of $LaFe_{11.03}Co_{0.80}Si_{0.94}Al_{0.23}$ compound exceeds that of Gd (9.8J/(kg·K) at T_{C}=293K) by as much as 70%. The full width at half maximum, δT_{FWHM}, defined as the temperature interval corresponding to the half maximum of $|\Delta S|$, is about 30 and 32K for the Co-free and Co-substituted samples, respectively.

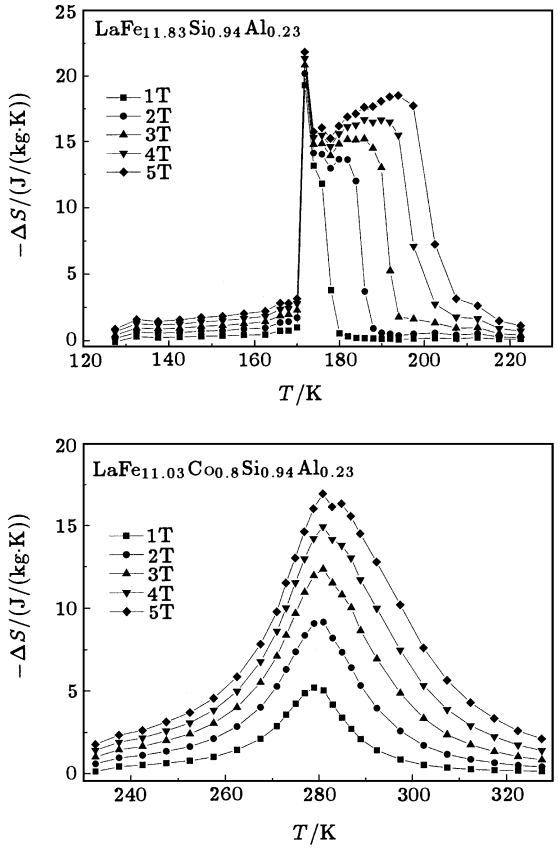


Fig.5. Temperature dependence of $|\Delta S|$ of $LaFe_{11.83}Si_{0.94}Al_{0.23}$ and $LaFe_{11.03}Co_{0.80}Si_{0.94}Al_{0.23}$ compounds under a change in magnetic field from 0 to 5T.

It was observed that the ΔS peak of the samples broadens asymmetrically with the increase of the applied field, as shown in Fig.5. It is believed that the field-induced metamagnetic transition above T_{C} contributes to the asymmetrical broadening of ΔS. Figure 6 shows the Arrott plots of the two samples, in which the appearance of the inflection point confirms the occurrence of a metamagnetic transition from the paramagnetic to ferromagnetic ordering above T_{C}. Indeed, a low field only drives the transition at the temperature near T_{C}, while a high field can drive the transition at the temperature much higher than T_{C}, which leads to a considerable entropy change at high temperature under high fields. Thus, the ΔS peak asymmetrically broadens to the high temperature side with increasing applied field.

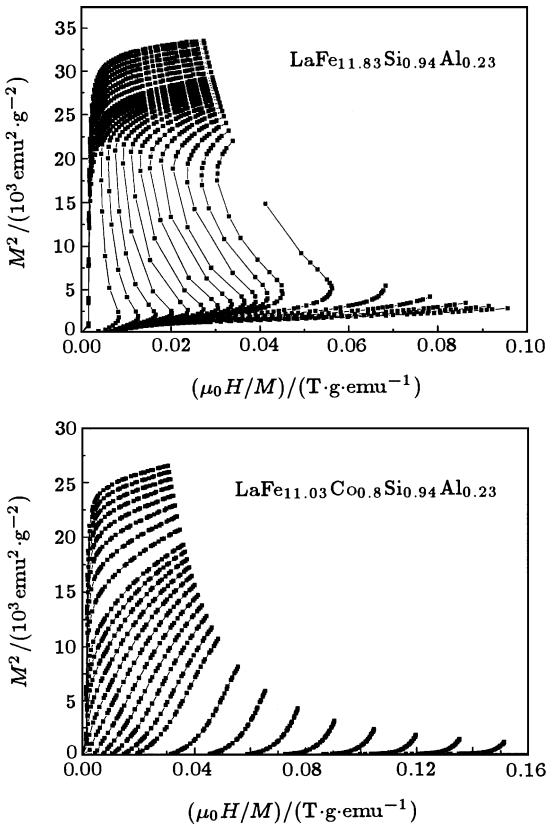


Fig.6. Arrott plots of $LaFe_{11.83}Si_{0.94}Al_{0.23}$ and $LaFe_{11.03}Co_{0.80}Si_{0.94}Al_{0.23}$ compounds.

The origin of the large magnetic entropy change in La–Fe–Si-based compounds can be attributed to the comparatively high 3d moments and the rapid change of magnetization in the field-induced magnetic phase transition. It can be confirmed from Fig.6 that the present compounds exhibit a first-order itinerant-electron metamagnetic (IEM) transition. The abrupt

change of magnetization near T_C is a striking characteristic of the first-order IEM transition, which has been studied in detail in La(Fe, Si)$_{13}$ compounds.[14] Previous studies have found that the La–Fe–Si compounds exhibit a large negative thermal expansion at T_C. The lattice parameter of $LaFe_{11.4}Si_{1.6}$ compound in the ferromagnetic state is larger than that in the paramagnetic state by ∼4‰ in the vicinity of the T_C, which is obtained by the measurement of the powder XRD patterns at different temperatures in the absence of a field. The abrupt change of magnetization at the T_C is caused by the dramatic negative lattice expansion. The coexistence of FM and PM phases around T_C had also been proved by neutron diffraction [15] and Mössbauer spectroscopy.[16] Discontinuous volume change and coexistence of two phases around T_C suggests that a first-order temperature-induced phase transition occurs.

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