J. Phys.: Condens. Matter **20** (2008) 135205 (5pp) doi:10.1088/0953-8984/20/13/135205

Effect of Si doping on the magnetic properties and magnetic entropy changes in the $LaFe_{11.4}Al_{1.6}$ intermetallic compound

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Received 17 October 2007, in final form 1 February 2008
Published 7 March 2008
Online at stacks.iop.org/JPhysCM/20/135205

Abstract

For $NaZn_{13}$-type $LaFe_{11.4}Al_{1.6-x}Si_x$ ($x = 0$–1.6) compounds, the lattice parameter linearly reduces with the increase of Si concentration. A mixture of antiferromagnetic phase and ferromagnetic clusters has been observed in the compound with $x = 0.22$. The magnetic phase diagram obtained from the isofield magnetization curves shows that the antiferromagnetic phase changes into the ferromagnetic phase at low temperature with increasing Si concentration. A spike-shaped magnetic entropy change has been found in the sample with $x = 0.3$, which is a spurious result obtained by using the Maxwell relationship. Meanwhile, a very broad plateau of magnetic entropy change is obtained, which is very favorable for a magnetic refrigerant. For the sample with $x = 0.8$, a large magnetic entropy change and very small hysteresis losses have been found due to the weak first-order phase transition.

1. Introduction

Magnetic refrigeration based on the magnetocaloric effect (MCE) of solid-state working substances has attracted tremendous attention in recent years due to their significant advantages over gas refrigerants [1, 2]. The MCE is characterized by the isothermal magnetic entropy change ΔS_M or the adiabatic temperature change arising from the application or removal of a magnetic field H on a system with magnetic degrees of freedom. The large magnetic entropy change in a $La(Fe, Si)_{13}$ system with a cubic $NaZn_{13}$-type structure has been intensively investigated [3–6]. The $LaFe_{11.4}Si_{1.6}$ compound shows $-\Delta S_M = 19.4$ J kg^{-1} K at its Curie temperature T_C for a field change of 0–5 T, due to a strong first-order ferromagnetic to paramagnetic phase transition near T_C [3].

The $LaFe_{13-x}Al_x$ compounds with x ranging from 1.04 to 7.02 crystallize in the cubic $NaZn_{13}$-type structure [7–10]. With the increase of iron concentration, mictomagnetic, ferromagnetic (FM), and antiferromagnetic (AFM) states are observed successively. It is FM and AFM for $1.82 \leqslant x \leqslant 4.94$ and $1.04 \leqslant x < 1.82$, respectively. Obviously, the ground state is AFM in $LaFe_{11.4}Al_{1.6}$, which is different from ferromagnetic $LaFe_{11.4}Si_{1.6}$. The substitute of Si for Al could bring about some interesting magnetic properties. In this present paper, we systemically investigate the structure and magnetic properties in $LaFe_{11.4}Al_{1.6-x}Si_x$ ($x = 0$–1.6) compounds, in addition to the MCE of the selected $LaFe_{11.4}Al_{1.6-x}Si_x$ with $x = 0.3$ and 0.8.

2. Experiments

Polycrystalline samples with the nominal composition $LaFe_{11.4}Al_{1.6-x}Si_x$ ($x = 0$–1.6) were prepared by arc melting appropriate amounts of starting materials (higher than 99.9% in purity) under ultrapure argon atmosphere (10 at.% excessive La was used to compensate the weight loss during the arc melting). The ingots were annealed in an evacuated quartz tube at 1223 K for 15 days for $x = 0$–0.4, 1273 K for 30 days for $x = 0.5$–0.8, 1273 K for 40 days for $x = 0.9$–1.5, and 1323 K for 50 days for $x = 1.6$, respectively. Powder x-ray diffrac-

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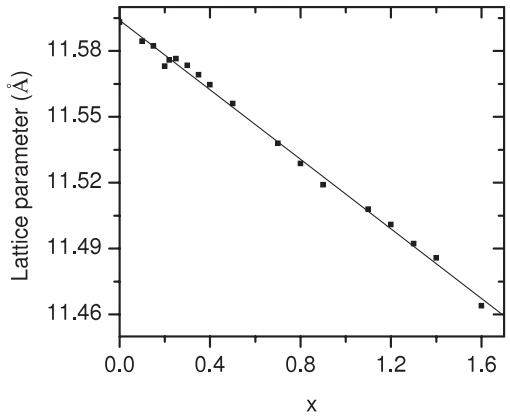

Figure 1. Si concentration dependence of the lattice parameter in $LaFe_{11.4}Al_{1.6-x}Si_x$ ($x = 0$–1.6) compounds. The solid line is the linear fitting result.

tion (XRD) was performed to characterize the crystal structure of the samples. Temperature dependent magnetization under the field of 0.1 T and isothermal magnetization at 5 K for the present compounds were carried out on a commercial MPMS-7 superconducting quantum interference device (SQUID) magnetometer (Quantum Design). Measurements of magnetization versus field at different temperature and ac magnetic susceptibility versus temperature with amplitude of the alternating field of 0.001 T at several frequencies were performed on a commercial physical property measurement system (PPMS, Quantum Design).

3. Results and discussion

XRD results at room temperature indicate that all the alloys crystallized in a single phase with the $NaZn_{13}$-type cubic structure except for the presence of a minor α-Fe phase in the alloys with $x = 1.1$–1.6. Figure 1 shows the dependence of the lattice parameter on the Si concentration of $LaFe_{11.4}Al_{1.6-x}Si_x$ ($x = 0$–1.6) compounds. It can be seen that the lattice parameter linearly reduces from 11.5932 Å for $x = 0$ to 11.4639 Å for $x = 1.6$, because of the smaller atomic radius of Si than that of Al.

Figure 2 presents the zero-field cooling (ZFC) temperature (T) dependence of magnetization (M) on heating under a field of 0.1 T for $LaFe_{11.4}Al_{1.6-x}Si_x$ ($x = 0$–1.6) compounds. When the concentration of Si is lower than 0.2, all the alloys are AFM below the Néel temperature ($T_N \sim 194$ K). However, a cusp at 102 K is observed for the alloy with $x = 0.22$ (see figure 2(a)), which means the appearance of FM concentration in the AFM matrix according to the results of ac magnetic susceptibility (see figure 3, below). Similar phenomena and opinions have been observed in Gd_5Ge_4 [11]. The FM state is observed at low temperature, and the FM-to-AFM-to-PM transition occurs with increasing temperature for $LaFe_{11.4}Al_{1.6-x}Si_x$ with $x = 0.25$–0.4 (see figure 2(b)). However, the FM state at low temperature directly transforms into the PM state with increasing temperature for $LaFe_{11.4}Al_{1.6-x}Si_x$ with $x = 0.5$–1.6 (see figure 2(c)).

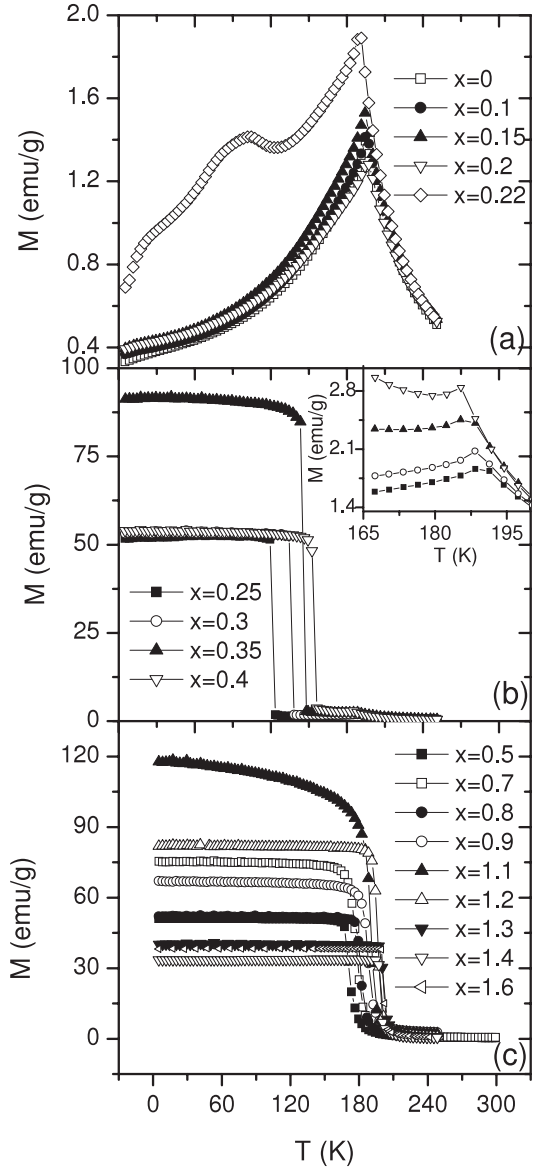

Figure 2. Temperature dependence of magnetization on heating in a field of 0.1 T of $LaFe_{11.4}Al_{1.6-x}Si_x$ ($x = 0$–1.6) compounds: (a) for $x = 0$–0.22; (b) for $x = 0.25$–0.4; and (c) for $x = 0.5$–1.6. The inset of (b) clarifies the details in the vicinity of the AFM–PM transition for $x = 0.25$–0.4.

Figure 3 shows the temperature dependence of the real part (χ') and imaginary part (χ'') of the ac magnetic susceptibility of the $LaFe_{11.4}Al_{1.6-x}Si_x$ ($x = 0.22$) compound, measured under a zero external dc magnetic field during heating the sample. There is a peak at ~102 K. This is in accord with the cusp shown in figure 2(a). A close view of the real part of the ac susceptibility around 102 K is displayed in the inset of figure 3(a). No frequency dependence of the peak position can be observed. Therefore, spin-glass freezing in zero dc H should be ruled out [12–14]. Simultaneously, the nonzero values of χ'' indicate the onset of an energy loss process, usually associated with domain dynamics, which is consistent with a weak ferromagnetism [15]. χ'' also exhibits a broad peak, indicating that some small ferromagnetic

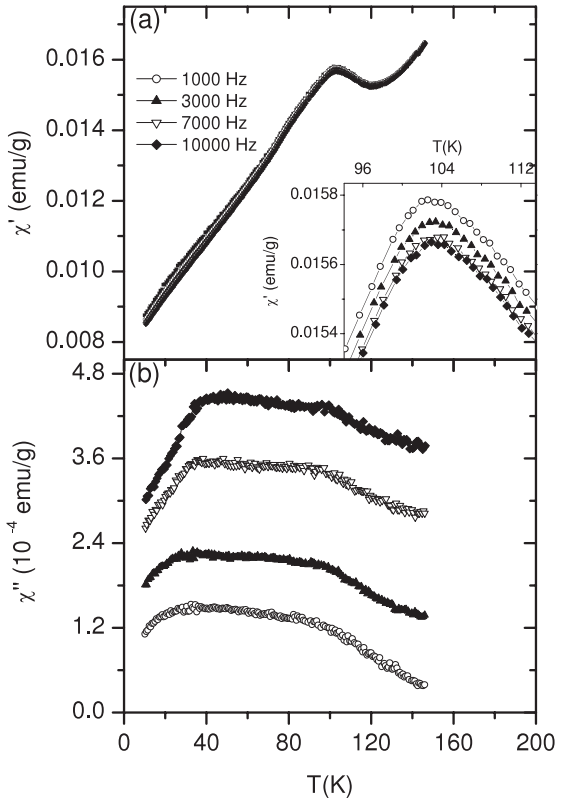

Figure 3. Temperature dependence of the real part (χ') and imaginary part (χ'') of the ac susceptibility of $Pr_{0.2}La_{0.8}Fe_{11.4}Al_{1.6}$, measured in a zero external dc magnetic field at typical frequencies (1000, 3000, 7000, and 10 000 Hz) during heating the sample: (a) χ'–T and (b) χ''–T. The inset plot of (a) clarifies details of the real part of the ac susceptibility around 102 K. T is varied with a sweep rate of 0.25 K min^{-1}.

clusters are formed [12]. In Gd_5Ge_4, this opinion has been confirmed by an *in situ* x-ray powder diffraction study [11]. Hence, the cusp at ∼102 K in the low-field ZFC M–T curves correlates well with the appearance of ferromagnetic component.

The magnetic phase transitions of $LaFe_{11.4}Al_{1.6-x}Si_x$ (x = 0–1.6) compounds with the concentration of Si are shown in figure 4, based on the zero-field-cooling isofield magnetization curves under a field of 0.1 T. The AFM-to-PM transition temperature, the FM-to-AFM transition temperature, and the FM-to-PM transition temperature are labeled as T_N, T_0, and T_C, respectively. As shown in figure 4, T_N slowly reduces, but T_0 and T_C enhance with the increase of Si concentration. The temperature range where FM clusters appear from the AFM background is indicated by an arrow for the compound with $x = 0.22$. So it can be concluded that the AFM phase gradually changes into FM phase at low temperature with the increase of Si concentration. In addition, magnetic field has a huge influence on the magnetic transition temperature for $x \leqslant 0.4$ due to the character of the first-order phase transition. For the compounds with $x = 0.25$–0.4, the increase of magnetic field reduces T_N and simultaneously enhances T_0. T_N and T_0 merge to T_C under a proper field. Namely, only FM-to-PM transition occurs directly when the applied field exceeds a certain value.

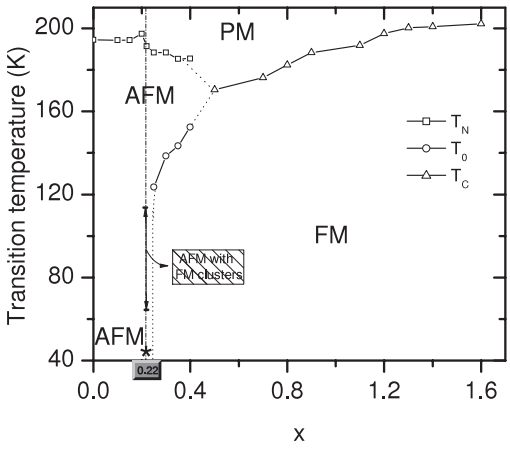

Figure 4. Magnetic phase diagram in $LaFe_{11.4}Al_{1.6-x}Si_x$ (x = 0–1.6) compounds. The solid lines and dotted lines indicate magnetic phase boundaries, and '↕' illustrates the temperature region where FM clusters appear from the AFM background for the compound with $x = 0.22$. The open symbols refer to magnetic phase transition temperatures.

The isothermal magnetization curves at 5 K are measured for these compounds. For $x \leqslant 0.22$, there is a sharp metamagnetic AFM–FM transition under a critical field. The saturation magnetizations of the FM state are obtained above the critical field according to the law of approach to saturation. For $x \geqslant 0.25$, the magnetization grows rapidly with increasing the field and then saturates directly, which indicates the characteristic ferromagnetic behavior in these compounds. Figure 5(a) displays the isothermal magnetization curves for the selected compounds. The variation of saturation magnetic moments of these compounds is exhibited in figure 5(b) based on the isothermal magnetization curves. One can find that it decreases slightly with increasing Si concentration. This indicates that the magnetic moment of 3d electrons of Fe is nearly unchanged by the substitution of Si for Al.

In $LaFe_{13-x}Si_x$ compounds, the external pressure makes the Curie temperature decrease [5, 6]. On the other hand, the FM ground state of the $La(Fe_{0.85}Al_{0.15})_{13}$ compound can be induced to the AFM state by increasing pressure [16]. Although the crystal lattice is also shrunk by the substitution of Si for Al, the variation of magnetic state with Si concentration is very different from that with the external pressure. Because the configuration of magnetic structure for the AFM $La(Fe, Al)_{13}$ compounds has not been very clear up to now [17], the mechanism for changes of magnetic properties induced by the substitution of Si for Al is still unknown.

As seen in figure 2(b), $LaFe_{11.4}Al_{1.6-x}Si_x$ compound with $x = 0.25$–0.4 shows similar and plentiful magnetic phase transitions with temperature increasing: an FM-to-AFM transition at low temperature, followed by an AFM-to-PM transition at high temperature. As an example, we focus on the MCE of the compound with $x = 0.3$. Its MCE is investigated based on the isothermal magnetization measurement. Figure 6 presents the magnetic entropy change as a function of temperature in typical field changes in the $LaFe_{11.4}Al_{1.6-x}Si_x$ ($x = 0.3$) compound. The entropy change is evaluated using the Maxwell relationship. In addition to

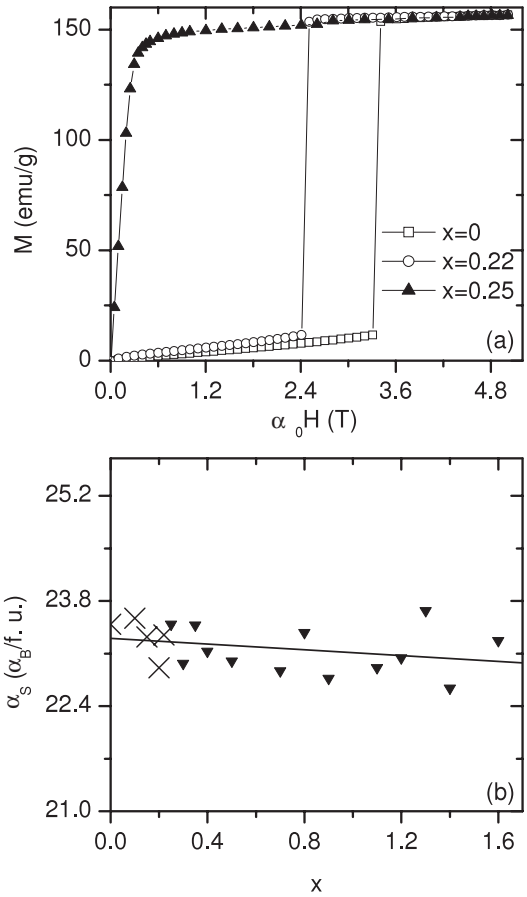

Figure 5. (a) Isothermal magnetization curves at 5 K for the selected compounds and (b) Fe concentration dependence of the saturated magnetic moments ('×' for the compounds with $x \leqslant 0.22$ and '▼' for the compounds with $x \geqslant 0.25$). The solid line in (b) is a guide to the eye.

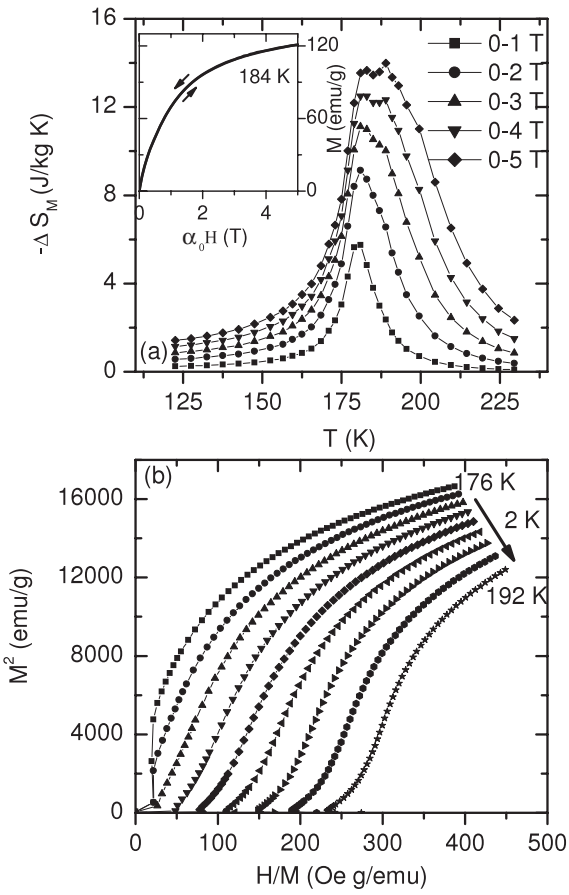

Figure 7. (a) Temperature dependence of the magnetic entropy change $-\Delta S_{\mathrm{M}}$ of $LaFe_{11.4}Al_{1.6-x}Si_x$ ($x = 0.8$) compounds for typical field changes and (b) Arrott-plots of this compound around T_{C}. Inset plot of (a): magnetization versus field curves for this compound at 184 K, arrows indicate the sequence of measurements.

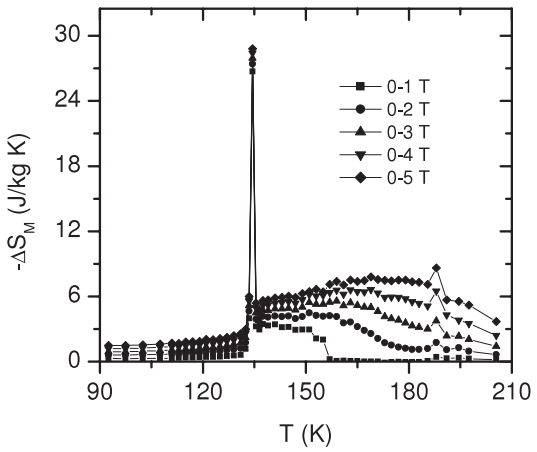

Figure 6. Temperature dependence of the magnetic entropy change $-\Delta S_{\mathrm{M}}$ of $LaFe_{11.4}Al_{1.6-x}Si_x$ ($x = 0.3$) compounds for typical field changes.

the flat plateau of the height of just several J kg^{-1} K, the magnetic entropy change for this compound is characterized by two peaks: one peak centered at T_{N} and one extra spike-shaped peak of 25–30 J kg^{-1} K centered round T_0. The width of the plateau in a field change of 0–5 T attains ∼70 K due to the superposition of the FM-to-AFM and AFM-to-PM phase transitions. This is very favorable for magnetic refrigeration. The emergence of the peak at T_{N} is correlated with the AFM–PM transition. However, the spike appears at T_0, which is an artifact [18] due to the evaluation of entropy change using the Maxwell relationship. A similar phenomenon has been observed in many other compounds such as MnAs under pressure [19], $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}$ [20], and $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ [18].

As shown in figure 2(c), $LaFe_{11.4}Al_{1.6-x}Si_x$ compounds with $x = 0.5$–1.6 display a simple FM–PM transition. So the MCE of $LaFe_{11.4}Al_{1.6-x}Si_x$ with $x = 0.8$ is investigated as the representative of compounds with $x = 0.5$–1.6. Figure 7(a) presents the temperature dependence of its magnetic entropy change in different field changes. The peak value of $-\Delta S_{\mathrm{M}}$ in a field change of 0–2 T is 9.1 J kg^{-1} K, which is much larger than that of Gd (5.0 J kg^{-1} K) [21]. However, it is lower than that of $LaFe_{11.4}Si_{1.6}$ in [3]. Arrott-plots [22] around T_{C} shown in figure 7(b) confirm that the nature of the phase transition for $LaFe_{11.4}Al_{1.6-x}Si_x$ ($x = 0.8$) is weak first-order, the same as that for $LaFe_{11.4}Si_{1.6}$ [3]. The hysteretic losses, which are very harmful to magnetic refrigeration, are

determined by computing the area inside the magnetization versus field loop. The inset plot of figure 7(a) gives the loop at 184 K (just 2 K above T_C). Obviously, the present compound has scarcely any hysteresis loss. The relatively large $-\Delta S_M$ of $LaFe_{11.4}Al_{1.6-x}Si_x$ ($x = 0.8$) compound in a relatively small field change (0–2 T), which can be supplied by a NdFeB permanent magnet, is favorable for practical applications.

Combining the magnetic entropy change of the selected compounds with the results in [3], one can find that the peak value of the $-\Delta S_M$ ascends with the increase of Si concentration under the same field change. This may be associated with the enhancement of the first-order phase transition, not with the saturated magnetic moments.

4. Conclusion

$LaFe_{11.4}Al_{1.6-x}Si_x$ ($x = 0$–1.6) compounds crystallize in the cubic $NaZn_{13}$-type structure. With the increase of Si concentration, the lattice parameter linearly reduces and the magnetic ground state changes gradually from AFM to FM states. A plateau-like $\Delta S_M(T)$ with a height of about 7 J kg^{-1} K has been found in a field change of 0–5 T for the sample with $x = 0.3$. The width of the plateau reaches ~70 K, which is very favorable for magnetic refrigeration. $LaFe_{11.4}Al_{1.6-x}Si_x$ ($x = 0.8$) compound with a weak first-order phase transition shows a large magnetic entropy change and very small hysteresis losses. Therefore, it is a very attractive candidate for a magnetic refrigerant in the corresponding temperature range.

Acknowledgments

This work was supported by the State Key Project of Fundamental Research and the National Natural Science Foundation (No. 10774178) of China.

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