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Nearly constant magnetic entropy change involving two closely spaced transitions in the compound $LaFe_{11.375}Al_{1.625}$

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Abstract

A large change in the magnetic entropy, $|\Delta S|$, was observed in the Fe-based $NaZn_{13}$-type compound $LaFe_{11.375}Al_{1.625}$, which was nearly temperature independent over a wide temperature range (an about 70 K span from ∼140 to 210 K). This behaviour of the magnetic entropy change is associated with two closely spaced magnetic transitions. X-ray diffraction investigation at different temperatures indicates that the crystal structure remains cubic, of $NaZn_{13}$ type, when the magnetic state changes with temperature, but the cell parameter changes dramatically at the first-order transition point.

1. Introduction

Recently, with the successful testing of a room-temperature magnetic refrigerator using a permanent magnet [1, 2] and the finding of new materials exhibiting a giant magnetocaloric effect (MCE) [3–5], the search for materials with a high MCE has been attracting much more attention. The ideal magnetic refrigerant suitable for use in an Ericsson-type refrigerator should have a constant (or almost constant) magnetic entropy change through the thermodynamical cycle range [6]. Thus the field-induced entropy change should be constant over a wide temperature range for optimum efficiency. In an attempt to deal with this problem, the techniques of multilayering and physical mixing were used [6, 7], where ferromagnetic (F)

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materials with varying Curie temperatures are layered or sintered. However, other problems arise—for example, solid-state reactions between constituent materials—resulting in altering of the expected temperature profile of the magnetic entropy change. A good choice for a suitable Ericsson-cycle refrigerant would be a single material with an appropriate $|\Delta S|$ profile. Typical materials with such properties are those of the series (GdEr)NiAl [8], in which the suitable working temperature range of magnetic refrigeration is from ∼10 to ∼80 K. However, at relatively high temperatures, no materials have been reported to show a table-like $|\Delta S|$ up to now.

The compounds with cubic $NaZn_{13}$-type structure have recently been suggested as appropriate materials for exploring in the search for efficient magnetic refrigerants, due to their excellent soft ferromagnetism and high magnetization [9–12]. More recently, a great magnetic entropy change has been observed in $La(Fe, Si)_{13}$ and its Co-doped counterparts [5]. Its origin is the strong structural and magnetic interplay in the compounds, characterized by a large negative thermal expansion at the Curie temperature T_C. For $La(Fe, Al)_{13}$ compounds, the magnetic ground state changes from mictomagnetic to ferromagnetic (F) and then to an antiferromagnetic (AF) state with increasing Fe content [13]. At the magnetic phase boundary between the F and the AF states we synthesized the compound $LaFe_{11.375}Al_{1.625}$, in which two successive transitions were observed. The magnetic order transition at 181 K (T_N) from antiferromagnetism to paramagnetism is second order in nature, while the other one at 140 K (T_0) from ferromagnetism to antiferromagnetism is first order. It is found that a low field below 1 T can induce a metamagnetic transition from an AF to a F state in the AF region, which implies that the magnetic free energy difference between the F and AF states is quite small in the $LaFe_{11.375}Al_{1.625}$ compound. Investigation of the magnetic entropy change $|\Delta S|$ indicates that the $LaFe_{11.375}Al_{1.625}$ compound shows a nearly constant $|\Delta S|$ over a wide temperature range from ∼140 to 210 K.

2. Experimental details

The ingots of the present sample were prepared by repeatedly arc-melting the appropriate amounts of the starting materials with purity of 99.9% and subsequent homogenized by annealing at 1273 K for 30 days. Measurements on the x-ray powder diffraction (XRD) pattern show that the $LaFe_{11.375}Al_{1.625}$ compound crystallized in a single phase of cubic $NaZn_{13}$-type structure. A little α-Fe impurity was observed, the amount of which is estimated to be 2 wt% on the basis of Rietveld refinement of the x-ray diffraction data. All magnetic measurements were performed using a superconducting quantum interference device (SQUID) magnetometer.

3. Results and discussion

The low-magnetic-field temperature-dependent magnetization has been measured in both zero-field-cooled (ZFC) and field-cooled (FC) processes in order to determine the magnetic state, the transition temperature, and the nature of the transition. The sample was first cooled in zero field to 5 K, then a small field was applied to the sample; after that the magnetization was measured while heating up to 300 K with the field fixed, and thus the ZFC magnetization curve was obtained. The FC magnetization was measured while cooling the sample to 5 K with the same field. Figure 1 presents the ZFC–FC magnetization of $LaFe_{11.375}Al_{1.625}$ obtained under a magnetic field of 0.01 T. Two successive transitions were found. The transition between antiferromagnetism and paramagnetism occurs at 181 K (T_N)—this is completely temperature reversible—while the other one, between ferromagnetism and antiferromagnetism, at 140 K

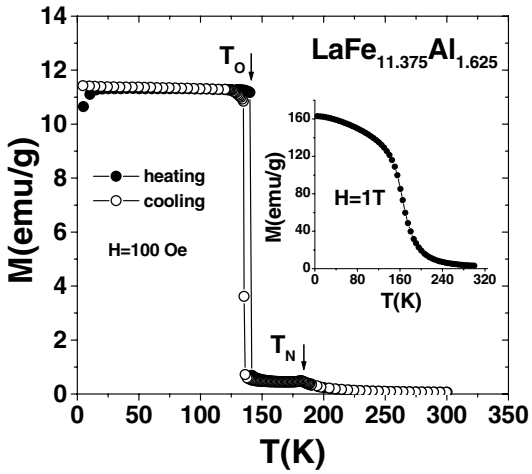

Figure 1. The ZFC–FC magnetization of $LaFe_{11.375}Al_{1.625}$ obtained under a magnetic field of 0.01 T. The inset shows the thermomagnetic curve measured under 1 T while heating.

(T_0, on heating) has a temperature hysteresis of ∼5 K. The behaviour of the ZFC–FC magnetization manifests first- and second-order natures for the transitions at T_0 and T_N, respectively. The inset of figure 1 shows the temperature-dependent magnetization measured under a field of 1 T in the heating process. The transition at T_0 is erased. This means that the weak AF coupling can be overcome by a 1 T field, which will cause the spin-flip transition to the F state. It is worth pointing out that the observed anomalous behaviour of the ZFC magnetization at low temperature is related to the existence of AF or F clusters [13]. It is known that La(Fe, Al)$_{13}$ compounds show mictomagnetic, F, and AF states with increasing Fe concentration. The competition between a nearest-neighbour Fe–Fe F exchange and a further-neighbour Fe–Al–Fe AF exchange always exists. With such coupling, the magnetic moments will be frozen in randomly at low temperature without long-range F or AF order [13].

We also performed measurements on XRD patterns at different temperatures in the heating process in order to check the change of the crystal structure. Figure 2 shows the temperature-dependent XRD at several selected temperatures. The peak marked by an asterisk in the pattern relates to the impurity α-Fe. One can see that the crystal structure of $LaFe_{11.375}Al_{1.625}$ remains cubic, of $NaZn_{13}$ type, while the magnetic state changes with temperature. The XRD pattern at 165 K (above T_0) is obviously shifted to larger 2θ compared with that at 80 K (below T_0), implying large thermal contraction of the lattice during the first-order transition. The small changes of the XRD patterns between 20 and 80 K, 165 and 240 K are hardly visible to the eye. The inset of figure 2 displays the deduced cell parameter, with an error limit of $\pm 1/1000$ Å, as a function of temperature. It is evident that the first-order transition at 140 K (T_0) accompanies a big jump in the cell parameter, while the change of the cell parameter for the second-order transition at 181 K (T_N) is very small (if there is any). The phenomenon of negative thermal expansion even below the transition temperature is in agreement with early reports [13, 16]. Figure 3 gives the Rietveld refinement results for two selected temperatures of 88 K (below T_0) and 240 K (above T_0), from which the amount of α-Fe impurity is estimated to be ∼2 wt%. The atom positions obtained for every atom are listed in table 1. In the $NaZn_{13}$-type structure [13] of $LaFe_{11.375}Al_{1.625}$, Fe atoms occupy two different sites, Fe^{I} (8b) and Fe^{II} (96i), while Al atoms occupy 96i positions. The Fe^{I} atoms are each surrounded by an icosahedron of twelve atoms of Fe^{II} and Al, while Fe^{II} atoms are surrounded by one Fe^{I} atom and nine atoms of Fe^{II}

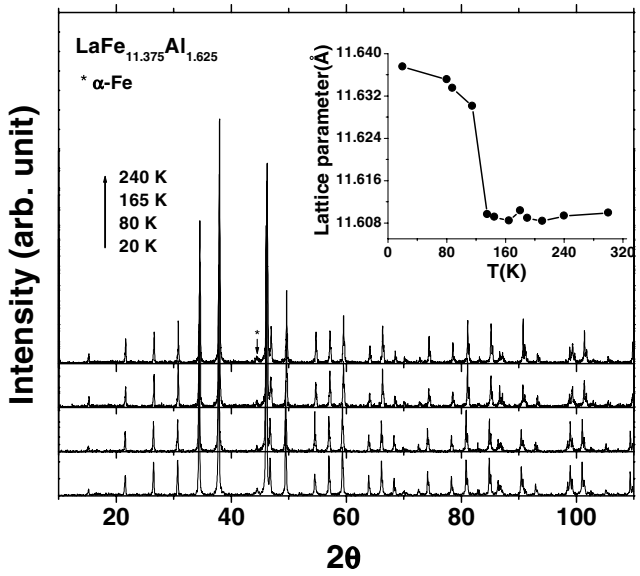

Figure 2. XRD patterns at temperatures of 20, 80, 165, and 240 K for $LaFe_{11.375}Al_{1.625}$. The inset shows the lattice parameter as a function of temperature.

Table 1. Atom positions and Fe^{I}–Fe^{II} and Fe^{II}–Fe^{II} distances at different temperatures in $LaFe_{11.375}Al_{1.625}$.

T	Atom	*x*	*y*	*z*	Fe^{I}–Fe^{II} distance (Å)	Fe^{II}–Fe^{II} distance 1 (Å)	Fe^{II}–Fe^{II} distance 2 (Å)	Fe^{II}–Fe^{II} distance 3 (Å)	Fe^{II}–Fe^{II} distance 4 (Å)
88 K	La (8a)	0.250 00	0.250 00	0.250 00					
	Fe^{I} (8b)	0.000 00	0.000 00	0.000 00					
	Fe^{II} (96i)	0.000 00	0.179 74	0.117 03	2.495	2.723	2.600	2.474	2.526
	Al (96i)	0.000 00	0.179 74	0.117 03					
240 K	La (8a)	0.250 00	0.250 00	0.250 00					
	Fe^{I} (8b)	0.000 00	0.000 00	0.000 00					
	Fe^{II} (96i)	0.000 00	0.178 94	0.116 79	2.481	2.712	2.583	2.479	2.530
	Al (96i)	0.000 00	0.178 94	0.116 79					

and Al. One Fe^{I}–Fe^{II} distance and four Fe^{II}–Fe^{II} distances were obtained in our sample. The detailed changes of the Fe^{I}–Fe^{II} and Fe^{II}–Fe^{II} distances upon phase transition can be found in table 1.

As is well known, FeRh and GdSiGe alloys undergoing a first-order phase transition show a giant MCE [17–19]. At the phase transition point, a discontinuity of the lattice parameter of FeRh is observed, while in GdSiGe alloys a change of symmetry from a monoclinic to an orthorhombic structure occurs. The simultaneous change in structure and magnetization at the transition temperature is responsible for the giant magnetic entropy change. In the following, we shall show that $LaFe_{11.375}Al_{1.625}$, with a first-order transition, also exhibits a large magnetic entropy change.

Figure 4(a) displays the magnetization isotherms of $LaFe_{11.375}Al_{1.625}$ measured up to 5 T on field increase over a wide temperature range from 90 to 235 K with a temperature

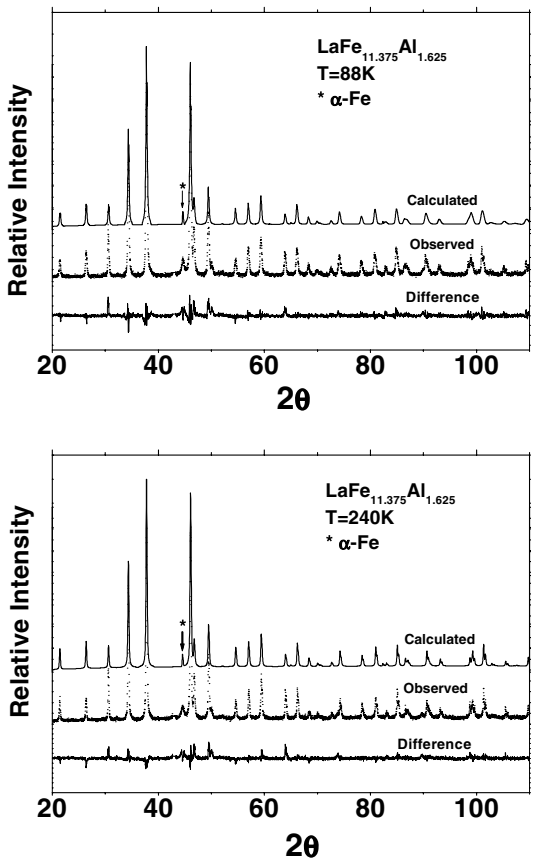

Figure 3. Rietveld refinement patterns for two selected temperatures, 88 and 240 K, for $LaFe_{11.375}Al_{1.625}$.

step of 5 K. Figure 4(b) shows the isotherms for field increase and decrease with a cycle from 0 to 2 T. The sweep rate of the field is slow enough to ensure that the isotherms are recorded isothermally. At low temperatures, these curves exhibit a characteristic F behaviour. The low-field magnetization becomes smaller above T_0. It should be noted that a sharp change of the magnetization with a hysteresis appears above a critical field H_C, which means that a field-induced first-order phase transition from an AF to a F state takes place. With increasing temperature the hysteresis width becomes narrower and the critical transition field H_C increases. A feasible model was proposed [14, 15] from considering the equilibrium state of the magnetic free energy as a function of magnetization, $f(M)$, which has a double minimum corresponding to the F and the AF states in the present system. The two states are separated by an energy barrier. In itinerant electron systems, $f(M)$ is renormalized by spin fluctuations at finite temperatures. With increasing temperature, spin fluctuations become larger and the free energy $f(M)$ of the F state is increased by the renormalization effect. The thermally induced transition between the F and AF states takes place when the free energy exceeds the maximum of the energy barrier. Also, a field-induced itinerant electron metamagnetic (IEM) transition from an AF to a F state occurs when the Zeeman energy drives the energy minimum of the F state lower than that of the AF state above T_0. With increasing temperature, the renormalization effect eliminates the energy barrier and the IEM disappears, showing that the hysteresis width

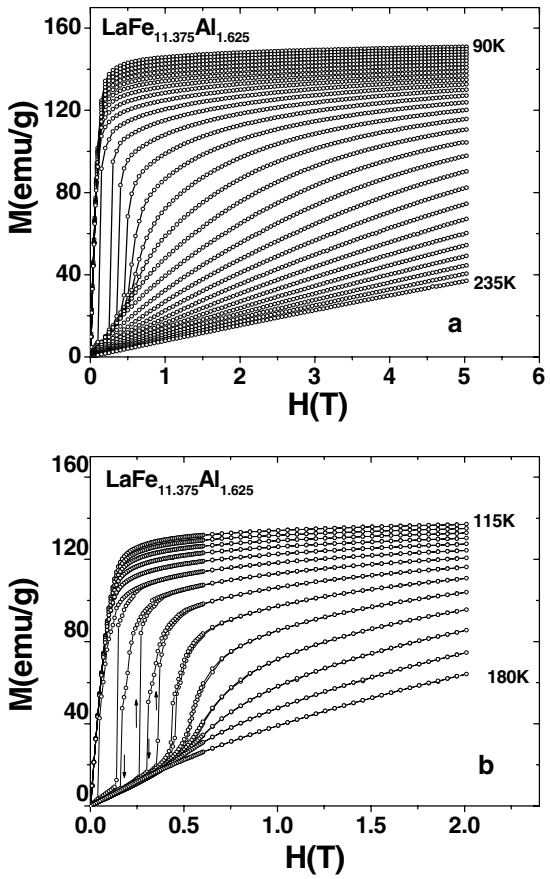

Figure 4. Magnetization isotherms of $LaFe_{11.375}Al_{1.625}$. (a) Isotherms for field increase up to 5 T. (b) Isotherms for field increase and decrease in a cycle from 0 to 2 T.

becomes narrower and even disappears. According to theoretical consideration [20], the critical field H_C as a function of temperature T can be expressed by using spin fluctuations $\xi(T)$:

$$H_C(T) = AM^3[\xi(T)^2 - \xi(T_0)^2]$$

where A is a constant, M is the magnetic moment, and T_0 is transition temperature. Theoretically, $\xi(T)^2$ is proportional to T^2 at low temperatures and changes to being proportional to T with increasing temperature [15, 21]. The Co-based Laves phase compounds which have an IEM transition at low temperatures usually show a T^2-dependence of H_C [21]. The H_C obtained in our experiments, defined as the average of the inflection points in the field-increase and field-decrease curves, is found to be linearly dependent on temperature, with a rate of $\mathrm{d}H_C/\mathrm{d}T \sim 0.023\ \mathrm{T\ K^{-1}}$. The linear increase of H_C against T should originate from $\xi(T)^2$ being proportional to T above T_0. In fact, the IEM transition of the present system occurs at relatively high temperatures compared to the case for the Co-based Laves phase compounds.

Figure 5 shows $\Delta S(H, T)$ calculated using the Maxwell relation [19, 22, 23] as functions of temperature and magnetic field. It is found that with increasing field, not only does the peak of ΔS at T_0 increase in magnitude, but also, importantly, its width notably increases towards higher temperature, which is a result of the field-induced metamagnetic transition from an AF to a F state above T_0 [5]. The overlap with the contribution from the second-order transition

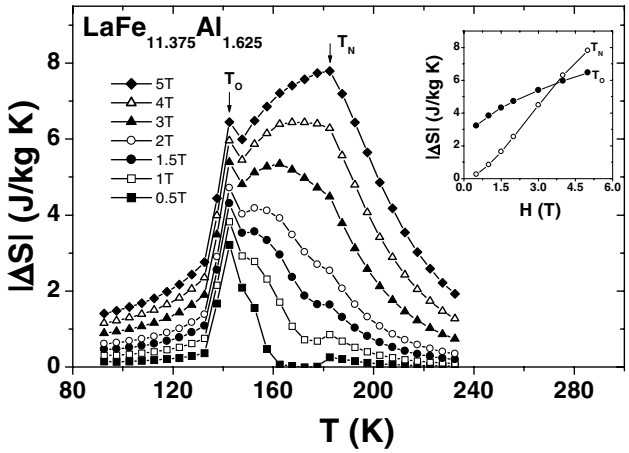

Figure 5. The magnetic entropy change $|\Delta S|$ of $LaFe_{11.375}Al_{1.625}$ under different fields. The inset depicts the magnetic entropy change as a function of applied field for the two transition temperatures T_N and T_0.

at higher T_N results in a nearly constant magnetic entropy change over a wide temperature span from ∼140 to 210 K, especially for fields around 3 T. The inset of figure 5 shows the magnetic entropy change at the two transition temperatures T_N and T_0 as a function of applied field. Obviously, the rate of increase of $|\Delta S|$ for the temperature T_N is bigger than that for the temperature T_0. The thermodynamic calculations [24] indicate theoretically that for an ideal first-order system, in which the transition occurs at a definite temperature, the peak values of the MCE in terms of both magnetic entropy change and adiabatic temperature change remain essentially constant, while the peak width increases with increasing temperature when the applied field increases. The magnitude of the magnetic entropy change ΔS is completely determined by the enthalpy change ΔE during the ideal first-order transition: $\Delta S = \Delta E/T$. ΔE is independent of the applied field [24]. However, due to the strong structural and magnetic interplay characterized by the big jump of the cell parameter at T_0 in the present real system, ΔE should be somewhat influenced by the applied field and increase with increasing field. This effect, combined with the contribution from the second-order transition at T_N, results in the present increase of $|\Delta S|$ at T_0 with increasing field. Also, the more rapid increase of ΔS at T_N should be ascribed to not only the second-order transition at T_N but also the field-induced metamagnetic transitions above T_0. It is easy to understand, for the second-order systems, the sensitivity of the magnetic entropy change to the applied magnetic field, considering the strong influence of the applied field on the spins.

The nearly table-like ΔS under a high field above 2.5 T and the high magnitude of ΔS under a low field below 1 T are the advantages of our compound. As mentioned in the introduction, a temperature-independent ΔS is desired for application in an Ericsson-cycle refrigerator. Also, the high magnitude of the low-field entropy change is of special interest for practical applications. For example, the $|\Delta S|$ peak value under a field of 0.5 T reaches the considerable magnitude of 3.2 J kg^{-1} K^{-1}. Since the cooling power per unit volume is a critical parameter for a magnetic refrigerator, we give the $|\Delta S|$ in volumetric units: 23 mJ cm^{-3} K^{-1} upon field change from 0 to 0.5 T. Although the peak value of $|\Delta S|$ (∼8 J kg^{-1} K^{-1} under a field of 5 T) in the present compound is somewhat smaller than the corresponding values (∼10–11 J kg^{-1} K^{-1} under 5 T) reported for LaFeCoAl compounds [10, 12], the temperature range (∼70 K) exhibiting large $|\Delta S|$ is wider than that for LaFeCoAl (∼50 K). For real application in magnetic

refrigeration, not only is a high magnitude of $|\Delta S|$ required, but also a wide temperature scale is important. In short, the nearly table-like $|\Delta S|$ with a considerable magnitude over a significant temperature range, caused by two successive transitions, is the main advantage of the present system compared with the $NaZn_{13}$-type systems previously reported on, which usually show a single phase transition and a λ-like or tower-like $|\Delta S|$ [5, 10, 12].

4. Summary

A nearly constant magnetic entropy change over a wide temperature range from ~140 to 210 K was observed in $LaFe_{11.375}Al_{1.625}$, involving two closely spaced magnetic transitions. Such behaviour of the magnetic entropy change is very favourable for application in an Ericsson-type refrigerator. The large magnitude of the magnetic entropy change mainly arises from the first-order nature of the transition from the AF to the F state accompanying an anomalous negative lattice expansion.

Acknowledgments

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