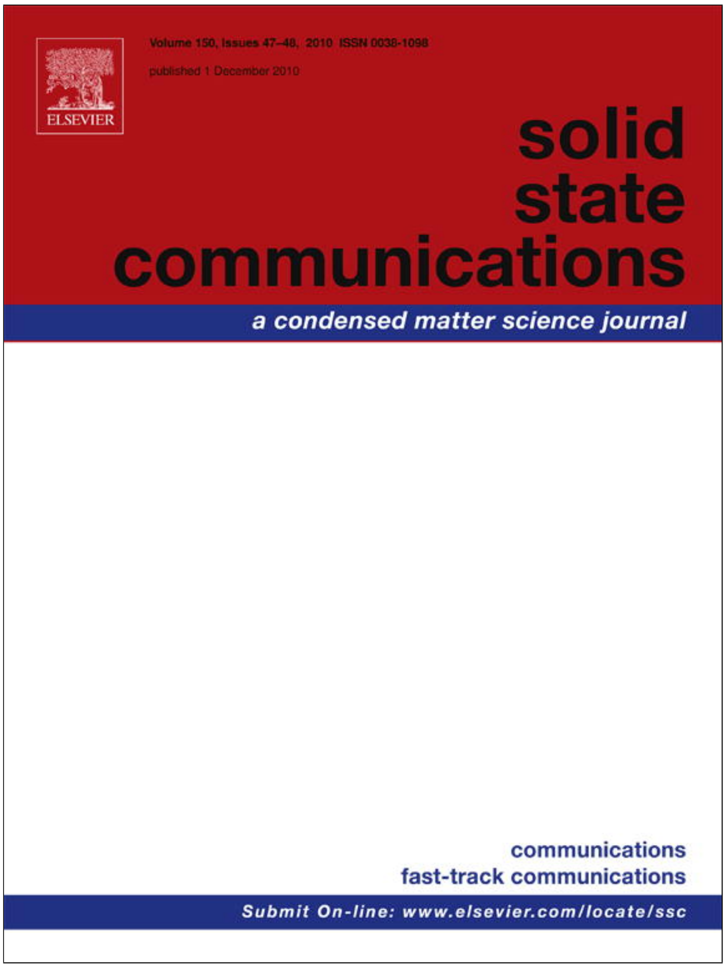

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Enhancement of the magnetocaloric effect and magnetic transition temperature in $LaFe_{11.5}Al_{1.5}$ by hydrogenation

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ABSTRACT

The magnetic properties and magnetocaloric effect (MCE) of $LaFe_{11.5}Al_{1.5}H_x$ ($x = 0.12$, 0.6 and 1.3) have been investigated. Introducing hydrogen atoms can drive the Curie temperature T_C to ambient temperature. The magnetic transition is changed from second order to weakly first order with increasing hydrogen content, leading to an increase in the magnetic entropy change ΔS_M. The maximal value of ΔS_M for $x = 1.3$ is determined to be 6.7 J/kg K at 295 K under a field change of 0–2 T. Good reversible MCE at low fields makes the hydrides promising room-temperature magnetic refrigerants.

1. Introduction

In the past few years, the search for room-temperature large magnetocaloric materials has been of special interest because of their potential application in magnetic refrigeration. Several materials with a giant magnetocaloric effect (MCE) have been discovered [1–4]. $NaZn_{13}$-type $La(Fe, Si)_{13}$-based compounds are among the most attractive magnetocaloric materials due to their outstanding performance with respect to MCE, tunable Curie temperature (T_C), and low cost; thus they show the potential of becoming a favorite working material near room temperature [5,6]. It has been reported that $LaFe_{11.4}Si_{1.6}$ shows a large magnetic entropy change (ΔS_M) of 19.4 J/kg K at 208 K under a field change of 0–5 T due to a first-order magnetic transition at T_C [2]. The Curie temperature could be adjusted by substituting some Fe by other elements and/or by introducing interstitial hydrogen or carbon atoms into $LaFe_{13-x}Si_x$. It has been reported that the appropriate substitution of Co for Fe in $LaFe_{13-x}Si_x$ compounds can cause the T_C to increase even to room temperature and the compounds to display a large ΔS_M, larger than or similar to that of Gd [7–10]. T_C increases from 195 to 250 K and ΔS_M decreases from 24.8 to 12.1 J/kg K in $LaFe_{11.6}Si_{1.4}C_x$ interstitial compounds with x increasing from 0 to 0.6 [11]. The interstitial insertion of hydrogen atoms into the $La(Fe, Si)_{13}$ lattice can increase T_C up to room temperature, while ΔS_M still remains a very large value [12–14].

$La(Fe_{1-x}Al_x)_{13}$ compounds with $0.08 \le x \le 0.12$ were found to exhibit a weak antiferromagnetic (AFM) coupling, which can be overcome by applying a field of a few Teslas or adjusting the Fe concentration, temperature, volume, and pressure in the compounds [15,16]. It has been confirmed that, by substituting Co for Fe [17,18], magnetic rare earths for La [19,20], or introducing interstitial H, N or C atoms [21–26], the magnetic ground state of $La(Fe, Al)_{13}$ compounds can be changed from the AFM state to a ferromagnetic (FM) state. Previous investigations found that $La(Fe_{0.98}Co_{0.02})_{11.7}Al_{1.3}$ exhibits a ΔS_M of 10.6 J/kg K under a field change of 0–5 T at 198 K [17]. A modest ΔS_M has also been observed in other $NaZn_{13}$-type $La(Fe, Al)_{13}$-based compounds: e.g., 9.0 J/kg K at $T_C = 303$ K for $La(Fe_{0.92}Co_{0.08})_{11.83}Al_{1.17}$ [18], 10.1 J/kg K at $T_C = 262$ K for $LaFe_{11.5}Al_{1.5}C_{0.5}$ [24], and 8.3 J/kg K at $T_C = 266$ K for $LaFe_{11.44}Al_{1.56}C_{0.6}$ [25] under a field change of 0–5 T. $La_{0.8}Nd_{0.2}Fe_{11.5}Al_{1.5}$ is found to undergo two magnetic phase transitions, which lead to a table-like ΔS_M peak (9.0 J/kg K) in a wide temperature range of 160–185 K for a field change of 0–5 T around the transition temperature [27]. Although the change in the magnetic ground state from AFM to FM by hydrogenation has been reported, accompanied by a significant increase in T_C [21], a study on the MCE of $La(Fe, Al)_{13}H$ has been lacking until now. In the present paper, we report the influence of interstitial hydrogen atoms on the magnetic phase transition and MCE in $LaFe_{11.5}Al_{1.5}$. A good reversible room-temperature MCE at low magnetic fields is obtained in $LaFe_{11.5}Al_{1.5}$ by hydrogenation.

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2. Experiments

Samples with the nominal composition of $LaFe_{11.5}Al_{1.5}$ were prepared by arc-melting the appropriate amounts of the starting materials in an atmosphere of argon gas. The purity of the elements was better than 99.9%. A subsequent annealing was carried out at 1223 K for two weeks and then the samples were quenched into liquid nitrogen. X-ray diffraction (XRD) analysis, using a Rigaku D/max-2400 diffractometer, showed that a single-phase sample was obtained with the $NaZn_{13}$-type structure. Hydrogenations of $LaFe_{11.5}Al_{1.5}$ were carried out at different hydrogen pressures in order to obtain certain hydrogen contents by solid–gas reaction at 623 K. The hydrogen contents in $LaFe_{11.5}Al_{1.5}H_x$ were determined by the ideal gas law ($PV = nRT$), where P is the hydrogen pressure, V is the volume of the sealed chamber, n is the number of moles of hydrogen in the chamber, R is the ideal gas constant, which equals 8.3145 J/mol K, and T is the temperature at which the initial compounds were annealed in hydrogen. The estimated error for hydrogen content is about 5 wt%. Magnetization was measured as a function of temperature and magnetic field around the Curie temperature by using a superconducting quantum interference device magnetometer from Quantum Design. By using the Maxwell relation $\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH$, ΔS_M was calculated based on the isothermal magnetization data. The sweep rate of the field was 0.015 T/s to ensure that the M–H curves could be recorded in an isothermal process.

3. Results and discussion

The XRD patterns show that the hydrogenation of $LaFe_{11.5}Al_{1.5}$ does not modify the $NaZn_{13}$-type crystal structure, and only leads to a lattice expansion. The lattice constant in $LaFe_{11.5}Al_{1.5}H_x$ is found to increase with x from $a = 1.1592(7)$ nm for $x = 0$ to $a = 1.1651(2)$ nm for $x = 1.3$; that is, the room-temperature lattice constant of $LaFe_{11.5}Al_{1.5}H_{1.3}$ is about 0.5% larger than that of $LaFe_{11.5}Al_{1.5}$. This result is comparable with $LaFe_{11.5}Si_{1.5}H_x$, in which the room-temperature lattice constant of the hydride for $x = 1.3$ ($a = 1.1528$ nm) is larger than that of the parent alloy $LaFe_{11.5}Si_{1.5}$ ($a = 1.1475$ nm) by about 0.46% [12]. Fig. 1 shows the temperature dependence of magnetization under a field of 0.01 T in zero-field-cooled and field-cooled processes for $LaFe_{11.5}Al_{1.5}H_x$ ($x = 0$, 0.12, 0.6 and 1.3). It is evident that the parent $LaFe_{11.5}Al_{1.5}$ compound undergoes a transition from an AFM state to a paramagnetic (PM) state at the Néel temperature $T_N = 201$ K (see the inset of Fig. 1). However, an FM-to-PM transition is observed in the hydrides at the respective T_C, which increases monotonically from 225 to 295 K with x varying from 0.12 to 1.3. This demonstrates that the magnetic ground state of $LaFe_{11.5}Al_{1.5}$ changes from the AFM state to the FM state upon hydrogenation. The AFM-to-FM transition is characterized by the multiple free-energy minima in relation to invar effects [28]. The free-energies in the FM and AFM states are almost the same in magnitude, being separated by an energy barrier which can easily be overcome by introducing hydrogen. For the Fe-rich rare-earth iron compounds, T_C depends usually on Fe–Fe direct exchange interactions. The Rietveld refinement for $LaFe_{11.5}Al_{1.5}H_x$ shows that the interatomic Fe–Fe average bond length increases with the increase of hydrogen content from 0.276(6) nm for $x = 0$ to 0.277(5) nm for $x = 1.3$. Therefore, one of the reasons for the increase in T_C with x for $LaFe_{11.5}Al_{1.5}H_x$ may be the increase in the interatomic Fe–Fe distance upon hydrogen insertion.

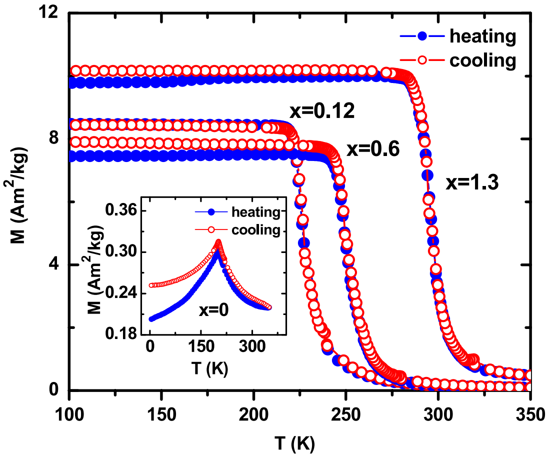

Fig. 1. Temperature dependence of the magnetization for $LaFe_{11.5}Al_{1.5}H_x$ ($x = 0.12$, 0.6 and 1.3) measured in heating and cooling processes under a magnetic field of 0.01 T. The inset shows the M–T curve of $LaFe_{11.5}Al_{1.5}$.

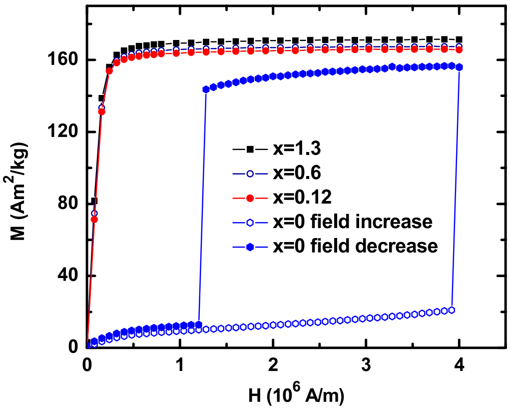

Fig. 2. Magnetization curves at 5 K for $LaFe_{11.5}Al_{1.5}H_x$ with $x = 0$, 0.12, 0.6 and 1.3.

Fig. 2 shows the magnetization curves of $LaFe_{11.5}Al_{1.5}H_x$ ($x = 0$, 0.12, 0.6 and 1.3) at 5 K. For the parent compound $LaFe_{11.5}Al_{1.5}$, the magnetization increases slowly with increasing field until a critical field about 4.9 T, when a sharp metamagnetic AFM-to-FM transition is observed. A large hysteresis occurs in field increase and decrease modes. A similar result has been observed in $LaFe_{13-x}Al_x$ [15,16,28]. However, the $LaFe_{11.5}Al_{1.5}H_x$ ($x = 0.12$, 0.6 and 1.3) compounds exhibit ferromagnetic behavior. The saturated magnetic moment is estimated from the M^2–H/M plots. It is found that the saturated magnetic moment has a remarkable increase from 1.99 μ_B/Fe to 2.12 μ_B/Fe with x increasing from 0 to 0.12. Further addition of hydrogen atoms leads to only a mild increase of the saturated magnetic moment. For $LaFe_{11.5}Al_{1.5}H_{1.3}$, the saturated magnetic moment is 2.19 μ_B/Fe.

From the above results, it is observed that the larger the lattice parameter, the higher the Curie temperature and the saturation magnetization, which indicate that the magnetic properties of the $LaFe_{11.5}Al_{1.5}H_x$ compounds are sensitive to volume change. The effects of hydrogen atoms on the magnetic properties of $LaFe_{11.5}Al_{1.5}H_x$ are mainly caused by 3d band narrowing. The lattice expansion caused by interstitial hydrogen atoms depresses the overlap between Fe 3d electrons, thus leading to an increase of magnetic moment and T_C.

For an itinerant-electron system at a finite temperature, the magnetic free energy is renormalized by the thermally excited spin fluctuations, accompanied by significant changes in magnetic properties. The renormalization of the free energy due to spin fluctuations may bring about further variation of magnetic phase transitions [28]. To verify the nature of the magnetic phase transition, the Landau coefficients in $LaFe_{11.5}Al_{1.5}H_x$ compounds with x ranging from 0.12 to 1.3 are calculated from the data of isothermal magnetization. The magnetic free energy based on

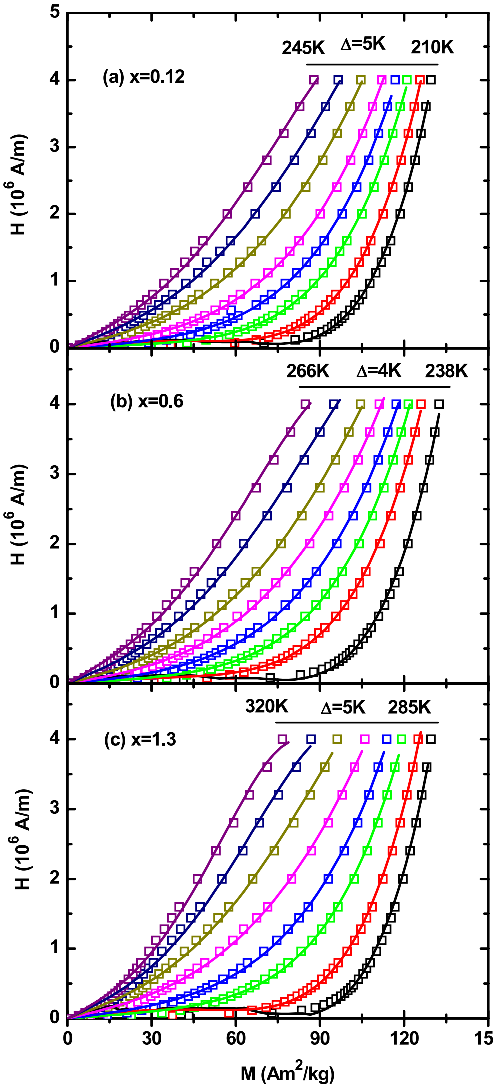

Fig. 3. Magnetization isothermal data around T_C for $LaFe_{11.5}Al_{1.5}H_x$ ((a) $x = 0.12$, (b) $x = 0.6$ and (c) $x = 1.3$) at different temperatures. The solid lines represent the fits to expression (3).

the Inoue–Shimizu model, $F(M, T)$, can well describe the phase transition, which can be expressed as a Landau expansion in the magnetization M [7,29]:

$$F(M,T) = \frac{1}{2}a_1(T)M^2 + \frac{1}{4}a_2(T)M^4 + \frac{1}{6}a_3(T)M^6 + \cdots - HM. \quad (1)$$

At the phase transition point, $F(M, T)$ reaches the minimal value

$$\frac{\partial F(M,T)}{\partial M} = 0. \quad (2)$$

So we get the following relationship:

$$H = a_1(T)M + a_2(T)M^3 + a_3(T)M^5. \quad (3)$$

The temperature dependence of the Landau coefficients $a_1(T)$, $a_2(T)$ and $a_3(T)$ can be obtained by fitting the isothermal magnetization data by using Eq. (3). The first coefficient $a_1(T)$ is the susceptibility, which must be positive and exhibits a minimum at T_C. The signs of $a_2(T)$ at T_C can be used to distinguish the first-order and second-order magnetic transitions; i.e., positive and zero values correspond to a second-order transition while a negative value corresponds to a first-order transition [7]. Fig. 3 shows the magnetization data near T_C together with the fitted curves for $LaFe_{11.5}Al_{1.5}H_x$ with $x = 0.12$, 0.6 and 1.3. It is found that the fitted

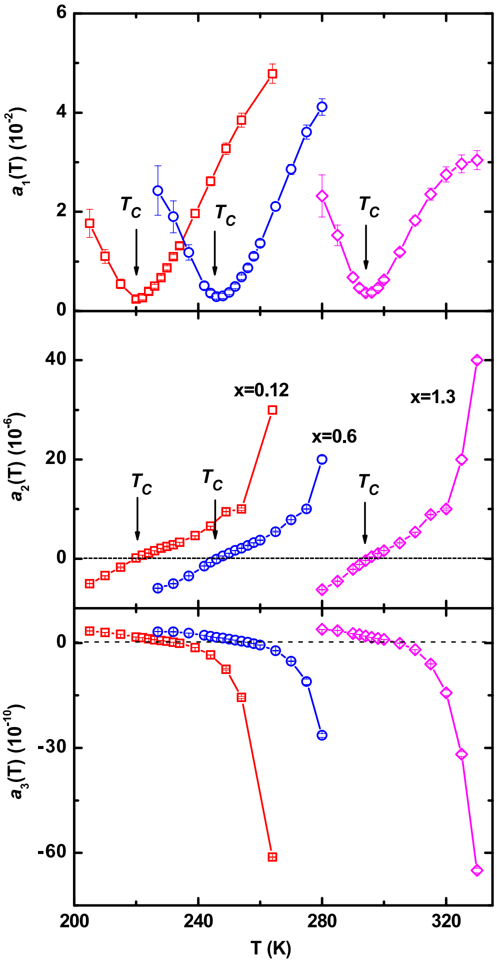

Fig. 4. Temperature dependence of Landau coefficients for $LaFe_{11.5}Al_{1.5}H_x$ (x = 0.12, 0.6 and 1.3). The units for $c_1(T)$, $c_2(T)$, and $c_3(T)$ are T^2kg/J, T^4kg^3/J^3, and T^6kg^5/J^5, respectively.

M–H curves in terms of the Landau model are in good agreement with the experimental data. This result indicates that the Landau model is appropriate to describe the magnetic phase transitions of $LaFe_{11.5}Al_{1.5}H_x$ compounds. The temperature dependence of the Landau coefficients derived from these fits is illustrated in Fig. 4 for $LaFe_{11.5}Al_{1.5}H_x$ with x = 0.12, 0.6 and 1.3. The values of $a_2(T)$ at T_C for x = 0.12, 0.6, and 1.3 are 0.12, −0.06, and −0.37, respectively, indicating that the magnetic transition at T_C is modified from second order to weakly first order with increasing hydrogen content. The hydrogenation of $LaFe_{11.5}Al_{1.5}$ may change the spin fluctuation, which plays an important role in the variation of magnetic phase transitions. The first-order magnetic transition obtained by introducing hydrogen atoms is expected to be capable of achieving a large ΔS_M for $LaFe_{11.5}Al_{1.5}H_x$.

The isothermal magnetization (M–H) curves of $LaFe_{11.5}Al_{1.5}H_x$ (x = 0.12, 0.6 and 1.3) were measured around T_C in a wide temperature range from 195 to 254 K for $x = 0.12$, 222 to 280 K for $x = 0.6$, and 270 to 320 K for $x = 1.3$. Fig. 3 gives the selective M–H curves of $LaFe_{11.5}Al_{1.5}H_x$ hydrides. Our results reveal that the isothermal M–H curves around T_C show a reversible behavior with magnetic field during the field increasing and decreasing processes, which is consistent with the fully reversible change of magnetization with temperature in the heating and cooling cycles near T_C, as shown in Fig. 1. These results indicate that the thermal and magnetic hystereses of $LaFe_{11.5}Al_{1.5}H_x$ are almost zero, which is highly desired in practical applications. ΔS_M as a function of temperature for $LaFe_{11.5}Al_{1.5}H_x$ is shown in Fig. 5. A negative peak around T_C can be observed from the ΔS_M–Tcurves,

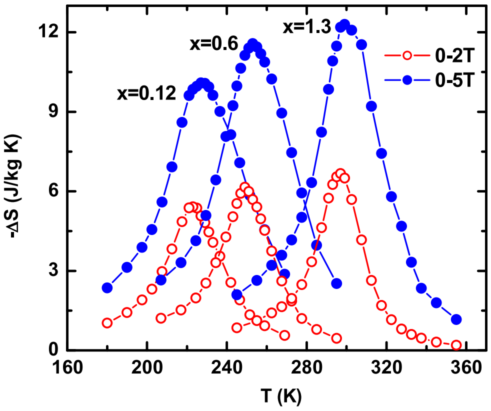

Fig. 5. Magnetic entropy change as a function of temperature for $LaFe_{11.5}Al_{1.5}H_x$ ($x = 0.12$, 0.6 and 1.3) for magnetic field changes of 0–2 T and 0–5 T, respectively.

and the maximal values of ΔS_M for $LaFe_{11.5}Al_{1.5}H_x$ ($x = 0.12$, 0.6 and 1.3) were determined to be 5.4, 6.2, and 6.7 J/kg K for a field change of 0–2 T, and 10.1, 11.6, and 12.3 J/kg K for a field change of 0–5 T, respectively. The ΔS_M value increases by about 22% as the hydrogen content x increases from 0.12 to 1.3. From the above results one can find that the increase in ΔS_M with increasing hydrogen content x in $LaFe_{11.5}Al_{1.5}H_x$ compounds is due to the larger saturation magnetic moment, and the nature of the magnetic phase transition at T_C changes from a second-order one to a first-order one caused by hydrogenation, as demonstrated by the change of the Landau coefficient $a_2(T)$ with x. It is interesting to note that the maximum values of ΔS_M for $LaFe_{11.5}Al_{1.5}H_{1.3}$ at $T_C = 295$ K for magnetic field changes of 0–2 T and 0–5 T, respectively, are 34% and 27% higher than those of Gd (5.0 and 9.7 J/kg K at 293 K for field changes of 0–2 T and 0–5 T, respectively) [6], which produces the highest MCE involving a second-order magnetic transition near room temperature. The ΔS_M values are also larger than those reported for $LaFe_{11.12}Co_{0.71}Al_{1.17}$ (4.5 and 9.0 J/kg K at $T_C = 303$ K) [18] and $LaFe_{11}Al_2C_{0.5}$ (3.3 and 6.3 J/kg K at $T_C = 291$ K) [23] under field changes 0–2 T and 0–5 T, respectively. The refrigerant capacity (RC) for $LaFe_{11.5}Al_{1.5}H_x$ ($x = 0.12$, 0.6 and 1.3) are calculated by numerically integrating the area under the ΔS_M–T curves (Fig. 5), with the temperatures at half maximum of the peak used as the integration limits [30]. The maximum values of RC for a field change of 0–5 T are found to be 406, 420, and 392 J/kg for $LaFe_{11.5}Al_{1.5}H_x$ with $x = 0.12$, 0.6, and 1.3, respectively. These values are comparable to those of $LaFe_{11.12}Co_{0.71}Al_{1.17}$ (410 J/kg at 5 T) [18], but much larger than those of $LaFe_{11}Al_2C_{0.5}$ (305 J/kg at 5 T) [23], where the RC values are estimated from the temperature dependence of ΔS_M in the respective literature.

4. Conclusions

In summary, the transition of the magnetic ground state from an AFM state to an FM state has been observed by introducing hydrogen atoms into the lattice in $LaFe_{11.5}Al_{1.5}$. Hydrogenation causes a shift of T_C towards higher temperatures, from 225 K for $x = 0.12$ to 295 K for $x = 1.3$, and a change in the order of the magnetic transition from second order to weakly first order. The ΔS_M value is found to increase with increasing hydrogen content. For $x = 1.3$, the maximal ΔS_M value is 12.3 J/kg K at 295 K, with a considerable RC value of 392 J/kg for a field change of 0–5 T.

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