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Magnetic entropy change and magnetic phase transition of $LaFe_{11.4}Al_{1.6}C_x$ (x=0–0.8) compounds*

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The unit cell volume and phase transition temperature of $LaFe_{11.4}Al_{1.6}C_x$ compounds have been studied. The magnetic entropy change, refrigerant capacity and the type of magnetic phase transition are investigated in detail for $LaFe_{11.4}Al_{1.6}C_x$ with x=0.1. All the $LaFe_{11.4}Al_{1.6}C_x$ (x=0–0.8) compounds have the cubic $NaZn_{13}$-type structure. The addition of carbon atoms brings about a considerable increase in the lattice parameter. The bulk expansion results in the change of phase transition temperature (T_c). T_c increases from 187 K to 269 K with x varying from 0.1 to 0.8. Meanwhile an increase in the lattice parameter can also cause a change of the magnetic ground state from antiferromagnetic to ferromagnetic. Large magnetic entropy change $|\Delta S|$ is found over a large temperature range around T_c and the refrigerant capacity is about 322J/kg for $LaFe_{11.4}Al_{1.6}C_{0.1}$. The magnetic phase transition belongs in weakly first-order one for x=0.1.

Keywords: $LaFe_{11.4}Al_{1.6}C_x$ compounds, magnetic phase transition, magnetic entropy change, refrigerant capacity

PACC: 7530S

1. Introduction

Nowadays, room-temperature magnetic refrigeration research has attracted much attention due to its high energy efficiency and environmental safety compared with the conventional vapour-cycle refrigeration.[1] Many attempts have been made to find appropriate refrigerants. Remaining large magnetic entropy change $|\Delta S|$ in a wide temperature range around room temperature is very important to evaluate refrigerants.[2,3] Gd is considered to be suitable for its large $|\Delta S|$ ($\sim$9.8 J·kg^{-1}·K^{-1}),[4] but it is too expensive. Up to now, materials with large $|\Delta S|$, such as $Gd_5(Si_xGe_{1-x})_4$, $MnFeP_yAs_{1-y}$, $La_{1-x}Ca_xMnO_3$ and $LaFe_{13-x}M_x$ (M=Al,Si) compounds,[5–14] have been found. Meanwhile, much effort has also been paid to investigate the effect of interstitial atoms (N, H and C) on $|\Delta S|$ in $LaFe_{13-x}M_x$ compounds for the improvement in Curie temperature T_c.[15–20] The corresponding hydrides and nitrides can only be synthesized by gas–solid reaction, and are metastable at room temperature. In contrast, the carbides of $LaFe_{13-x}M_x$ compounds can be directly prepared by arc melting and are stable at least up to 1000 K. Thus, the carbides may be suitable for room temperature magnetic refrigeration.

Previous research shows that $LaFe_{13-y}Al_y$ compounds have an antiferromagnetic ground state for $1.04 \leq y \leq 1.82$ and the magnetic ground state can be changed into a ferromagnetic one by introducing carbon atoms.[15,16,21] In this work, the influence of C atoms in $LaFe_{11.4}Al_{1.6}$ compounds on unit cell and magnetic phase transition temperature is studied intensively. Besides, a good refrigerant capacity is found in $LaFe_{11.4}Al_{1.6}C_{0.1}$ compounds and the type of its magnetic phase transition is investigated in several ways.

2. Experimental procedure

$LaFe_{11.4}Al_{1.6}C_x$ (x=0–0.8) compounds were pre-

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pared by arc melting in a high-purity argon atmosphere. The purity of element was higher than 99.9%. The samples were vacuum annealed for 13 days at 1223 K. The structural studies were carried out by the x-ray powder diffraction measurements using Cu $K\alpha$ radiation. Magnetic measurements were performed on a commercial MPMS-7 superconducting quantum interference device (SQUID) magnetometer.

3. Results and discussion

3.1. The influence of C on the unit cell volume and phase transition temperature of $LaFe_{11.4}Al_{1.6}$

The room temperature x-ray diffraction (XRD) patterns of $LaFe_{11.4}Al_{1.6}C_x$ (x=0–0.8) compounds indicate that all the samples have $NaZn_{13}$-type cubic structure, though there exists a small amount of α-Fe for x=0.8. The lattice parameter a of $LaFe_{11.4}Al_{1.6}C_x$ (x=0–0.8) compounds increases from 11.597Å to 11.648Å monotonically with x varying from 0 to 0.8. As reported in previous studies,[18,19,22] carbon atoms occupy the interstitial hole sites at 24d, which results in an increase in the Fe_1-Fe_1 and Fe_2-Fe_2 distance and thus a maximal bulk expansion of about 1.33%. Generally, the bulk expansion caused by carbonization reduces the overlap of the Fe 3d wave functions and makes the 3d band narrow, which may bring about an increase in T_c. On the other hand, the hybridization between the electronic orbits of C and Fe 3d in $LaFe_{13-y}Al_y$ carbides tends to decrease the value of T_c.[23–25] Figure 1 shows the thermal magnetic curves in a magnetic field μ_0H of 0.01 T. T_c increases from 187 K to 269 K when x changes from 0.1 to 0.8, which indicates that the bulk expansion effect is stronger than the hybridization effect. Although T_c can be enhanced by adding more carbon atoms, the nearly single-phased samples cannot be obtained yet for $x \geq 0.8$. So the value of T_c for $LaFe_{11.4}Al_{1.6}C_x$ compounds is limited to a maximum of 269K.

As shown in Fig.1, the magnetic ground state of antiferromagnetic $LaFe_{11.4}Al_{1.6}$ compound is changed to the ferromagnetic state when $x \geq 0.1$, which agrees with previous reports.[15,16] The antiferromagnetic interaction between Fe atoms is broken by increasing the Fe-Fe distance, which is caused by the addition of carbon atoms, and the magnetic ground state is changed to ferromagnetism accordingly.[15,26]

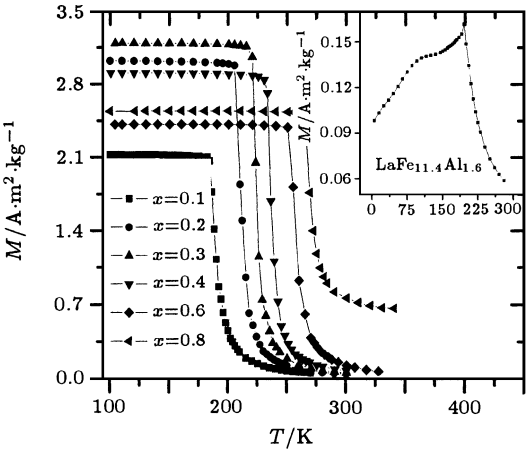


Fig.1. Thermal magnetic curves of $LaFe_{11.4}Al_{1.6}C_x$ in a magnetic field $\mu_0 H$ of 0.01 T. Insertion: Thermal magnetic curves of $LaFe_{11.4}Al_{1.6}$ in a magnetic field $\mu_0 H$ of 0.01T.

To show the influence of Al atoms, the variations of T_c with the lattice parameter a for $LaFe_{11.4}Al_{1.6}C_x$ and $LaFe_{11.5}Al_{1.5}C_x$[16] are displayed in Fig.2. The corresponding slope (1858K/Å) of linear relationship for $LaFe_{11.4}Al_{1.6}C_x$ is the same as that for $LaFe_{11.5}Al_{1.5}C_x$. It is well known that the atomic radius of Al is larger than that of Fe. As a consequence, the value of lattice parameter of $LaFe_{11.4}Al_{1.6}$ is larger than that of $LaFe_{11.5}Al_{1.5}$.[25] Thus, it can be used to understand the fact that the value of lattice parameter of $LaFe_{11.4}Al_{1.6}C_x$ is larger than that of $LaFe_{11.5}Al_{1.5}C_x$ with the same x for $x < 0.3$ in this work. Besides, it is obviously found that T_c of $LaFe_{11.5}Al_{1.6}C_x$ is lower than that of $LaFe_{11.5}Al_{1.5}C_x$ when x is the same. It suggests that the hybridization effect, which weakens the ferromagnetic interactions and cause a decrease in T_c, is stronger than the bulk expansion effect for the substitution of Al.

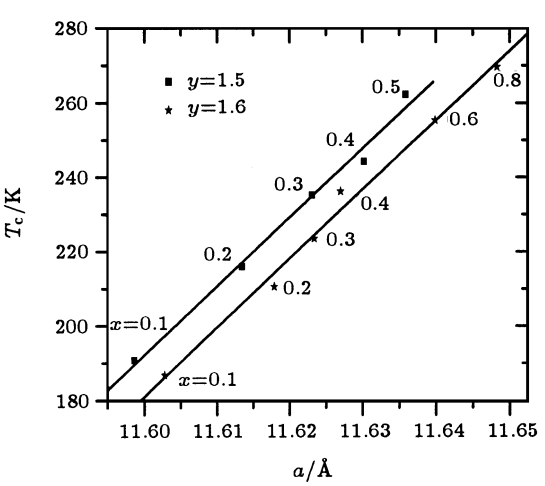


Fig.2. The dependence of T_c on the lattice parameter a for $LaFe_{13-y}Al_yC_x$ compounds with y=1.5 and y=1.6. The data for y=1.5 is cited from Ref.[16].

3.2. Magnetic entropy change and refrigerant capacity of $LaFe_{11.4}Al_{1.6}C_{0.1}$

The magnetic entropy change is calculated from one of the Maxwell's relationships $\Delta S(T,H) = -\int (\partial M/\partial T)_H \mathrm{d}H$.[27] Figure 3 shows the temperature-dependent magnetic entropy change under a magnetic field change of 0–5T. These data are obtained from the isothermal M-H data of $LaFe_{11.4}Al_{1.6}C_{0.1}$. The temperature step is 3K in the vicinity of T_c and 5K in a region far from T_c. The entropy change of $LaFe_{11.4}Al_{1.6}C_{0.1}$ ($|\Delta S|$ ~8.6 $J\cdot kg^{-1}\cdot K^{-1}$) is lower than that of $LaFe_{11.4}Al_{1.5}C_{0.1}$ ($|\Delta S|$ ~9.6 $J\cdot kg^{-1}\cdot K^{-1}$),[16] but it remains almost the same values in a wide temperature range.

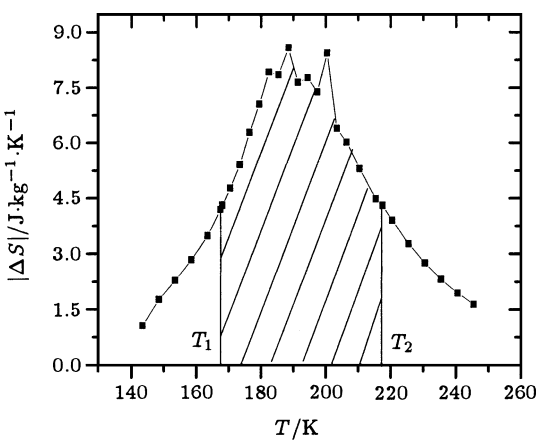


Fig.3. Temperature-dependent magnetic entropy change $|\Delta S|$ under a magnetic field change of 0–5T for $LaFe_{11.4}Al_{1.6}C_{0.1}$.

The temperature interval, starting at T_1 and ending at T_2 where the value of $|\Delta S|$ is half of its maximum,[28] is larger than that of $LaFe_{11.4}Al_{1.5}C_{0.1}$.[16] The value of q, which is estimated by the equation $q = -\int_{T_1}^{T_2} \Delta S \mathrm{d}T$ to evaluate the refrigerant capacity,[29] is about $322 J\cdot kg^{-1}$ for $LaFe_{11.4}Al_{1.6}C_{0.1}$. Comparing with $305 J\cdot kg^{-1}$ for $Gd_5Ge_2Si_2$,[30] $LaFe_{11.4}Al_{1.6}C_{0.1}$ has a good refrigerant capacity.

3.3. The type of magnetic phase transition in $LaFe_{11.4}Al_{1.6}C_{0.1}$

According to Ref.[31], the field-dependent $|\Delta S|$ at T_c can be expressed as

$$|\Delta S| = c(\mu H/k_B T_c)^{2/3} + d, \qquad (1)$$

where c and d are simulation parameters, $(\mu/k_B T_c)^{2/3}$ is a constant as long as T_c is determined, and $\mu \cong 2\mu_B$.

Figure 4 shows the dependence of the maximum $|\Delta S|$, i.e. the value of $|\Delta S|$ at T_c, on $(\mu H/k_B T_c)^{2/3}$. Obviously, it well agrees with the 2/3 power law mentioned above when H is not too low. The value of d (=$-1.63 J\cdot kg^{-1}\cdot K^{-1}$) is negative, which is similar to that for a second-order phase transition as reported in Ref.[31]. However, the value of c (=95.6 $J\cdot kg^{-1}\cdot K^{-1}$) is as small as that for a first-order phase transition.[31] To verify the type of phase transition in $LaFe_{11.4}Al_{1.6}C_{0.1}$, further investigations should be carried out.

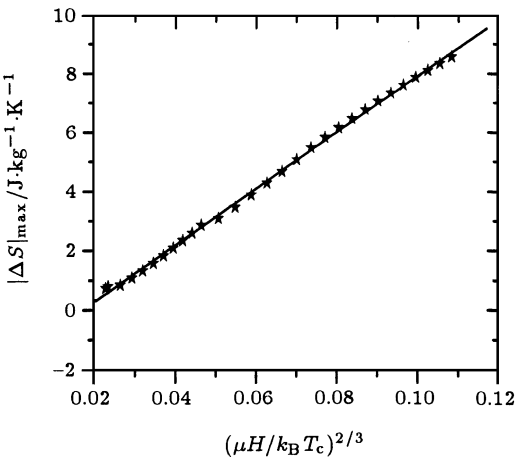


Fig.4. The maximum $|\Delta S|$ vs $(\mu H/k_B T)^{2/3}$ plot of $LaFe_{11.4}Al_{1.6}C_{0.1}$ compound.

As reported in Ref.[32], the magnetic free energy F can be expanded as a power series of M like

$$F = (1/2)[a_1 - \alpha(M)]M^2 + (1/4)a_3 M^4 + (1/6)a_5 M^6 + \cdots, \qquad (2)$$

where M is the magnetization. Then the magnetic field is given by

$$H = \partial F/\partial M = (a_1 - \alpha)M + a_3 M^3 + a_5 M^5 + \cdots, \qquad (3)$$

where a_1, a_3 and a_5 are Landau coefficients. It has been pointed out in this reference that the order of magnetic transition can be determined by the signs of coefficients $(a_1 - \alpha)$, a_3 and a_5. When $(a_1 - \alpha) > 0$, the ferromagnetism can be stable if $a_3 < 0$ and $a_5 > 0$. With the increase of temperature the spontaneous magnetization will vanish discontinuously at a certain temperature that is the very phase transition temperature T_c. This phase transition is defined as first-order phase transition. The condition of second-order phase transition is $a_3 > 0$ when $(a_1 - \alpha)$ exhibits a minimum at T_c . By fitting the magnetic field against the magnetization using the expression (3), the temperature-dependent coefficients $(a_1 - \alpha)$, a_3 and a_5 are displayed

in Fig.5. As shown in the figure, coefficient $(a_1 - \alpha)$ is positive and has a minimum at T_c. a_3 changes its sign from negative to positive with the increase of temperature. In the temperature region $T < T_c$, $a_3 < 0$ and the sign of a_5 is positive, namely $a_5 > 0$. According to Ref.[33], the phase transition in $LaFe_{11.4}Al_{1.6}C_{0.1}$ should belong in a first-order one rather than a second-order one.

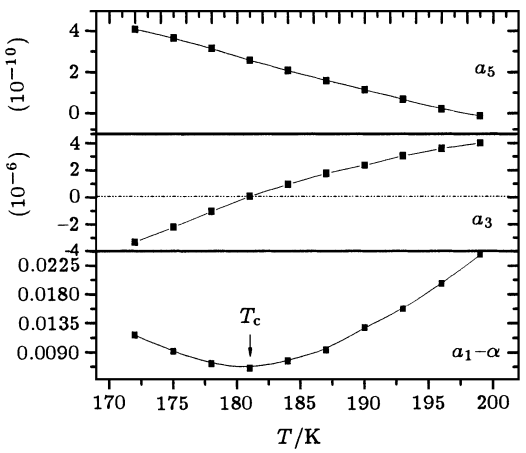


Fig.5. Temperature-dependent Landau coefficients for $LaFe_{11.4}Al_{1.6}C_{0.1}$.

Figure 6 show the Arrott plots of $LaFe_{11.4}$ $Al_{1.6}$ $C_{0.1}$. The M^2 versus H/M plot above T_c is characterized as S-shaped one, which confirms a first order phase transition in $LaFe_{11.4}Al_{1.6}C_{0.1}$ at its T_c,[33] while this S-shaped curve tends to be stretched to a straight line, implying that it is a weakly first-order phase transition in $LaFe_{11.4}Al_{1.6}C_{0.1}$.

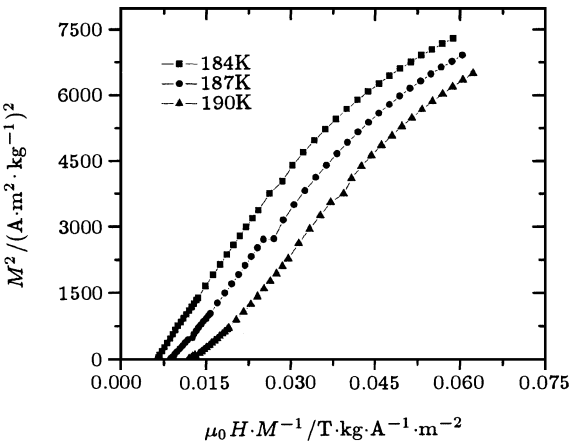


Fig.6. The Arrott plots at T_c and $T_c \pm 3$K of $LaFe_{11.4}Al_{1.6}C_{0.1}$ compound.

4. Conclusions

The addition of carbon atoms brings about an increase in lattice parameter, which results in the enhancement of T_c and the change of magnetic ground state of the parent compound $LaFe_{11.4}Al_{1.6}$. Antiferromagnetic interaction in $LaFe_{11.4}Al_{1.6}$ is broken due to the increase in the lattice parameter caused by carbonization, and thus the magnetic ground state is changed to ferromagnetic one. Large values of q make the carbides of $LaFe_{11.4}Al_{1.6}$ a candidate for refrigerant. The dependence of $|\Delta S|_{\max}$ on $(\mu_0 H)^{2/3}$ for $LaFe_{11.4}Al_{1.6}C_{0.1}$ agrees with the $H^{2/3}$ law. Due to the negative intercept of $|\Delta S|_{\max}$ vs $(\mu H)^{2/3}$ plot, S-shaped Arrott plot and the signs of Landau coefficients, the phase transition for $LaFe_{11.4}Al_{1.6}C_{0.1}$ should belong in a weakly first-order one.

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