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Magnetism and magnetic entropy change in $LaFe_{11}Al_2C_x$ compounds around room temperature*

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Magnetism and magnetic entropy changes in $LaFe_{11}Al_2C_x$ (x=0.0, 0.2 and 0.5) compounds have been investigated. The Curie temperature T_C is conveniently controlled from 200K to room temperature by varying the carbon concentration. Large magnetic entropy change is obtained over a wide temperature range due to the high magnetization and the drastic decrease in the magnetization around T_C. The large magnetic entropy change in wide temperature range, low cost and the convenience of controlling T_C suggest that the $LaFe_{11}Al_2C_x$ compounds are promising candidates for magnetic refrigerants in the corresponding temperature range.

Keywords: magnetic entropy change, $La(Fe_xAl_{1-x})_{13}$ interstitial compounds
PACC: 7530S

1. Introduction

Magnetic refrigeration (MR) research near to room temperature has attracted much attention in recent years due to its potential applications with higher energy efficiency and environmental safety in comparison with conventional gas refrigeration.[1−14] The rare earth Gd has long been thought to be the most suitable refrigerant near room temperature.[7] Some interesting materials, however, such as rare-earth compounds $Gd_5(Ge_{1-x}Si_x)_4$ ($0.2 \leq x \leq 0.5$),[4,5] polycrystalline perovskite manganese oxides [2,3,6,11] and the 3d transition compound $MnFeP_{1-x}As_x$ ($0.15 \leq x \leq 0.66$) [14] and $MnAS_{1-x}Sb_x$ [12] show a giant magnetocaloric effect (MCE).

Recently, the pseudobinary rare-earth transition compounds of the $La(Fe_xAl_{1-x})_{13}$ and $La(Fe_xSi_{1-x})_{13}$, crystallized in a cubic $NaZn_{13}$-type structure, have been found to exhibit large magnetic entropy change around the Curie temperature T_C.[15−18] The T_C of these compounds, however, is far below the room temperature. Previous studies have shown that nitrogen and hydrogen absorptions into $La(Fe_xAl_{1-x})_{13}$ and $La(Fe_xSi_{1-x})_{13}$ compounds give rise to volume expansion and in this way enhance their magnetic ordering temperature.[19−21] So, one can increase T_C of these compounds up to room temperature by introducing interstitial atoms. Chen and Fujita and colleagues have successfully obtained large magnetic entropy changes in $La(Fe_xSi_{1-x})_{13}H_y$ [18,22−24] and $La(Fe_xSi_{1-x})_{13}C_y$ [25,26] interstitial compounds around room temperature by introducing the interstitial atoms hydrogen and carbon.

In the present study, the carbide $LaFe_{11}Al_2C_x$ was first prepared via simple solid–solid reactions, and the magnetism and magnetic entropy change were investigated.

2. Experiment

$LaFe_{11}Al_2C_x$ (x=0.0,0.2 and 0.5) compounds were prepared by arc melting the appropriate raw materials in an Ar gas atmosphere and followed by annealing for two weeks at 950°C for homogenization. X-ray diffraction (XRD) measurements on powder samples using Cu $K\alpha$ radiation were performed to examine the phase purity and to determine the crys-

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tallographic structure. Magnetic measurements were performed on a commercial MPMS-7 type superconducting quantum interference device (SQUID) magnetometer.

3. Results and discussion

Figure 1 shows the XRD patterns of $LaFe_{11}Al_2C_x$ compounds with x=0.0,0.2 and 0.5. All samples crystallize in a single phase of the cubic $NaZn_{13}$-type structure ($Fm3c$) at room temperature. The peak positions, however, shift to lower angles with the increase of carbon concentration, suggesting the expansion of the lattice parameter a. The value of a is 1.16142, 1.16446 and 1.16821nm for x=0.0, 0.2 and 0.5 respectively. Previous studies in the $La(Fe_xAl_{1-x})_{13}$ interstitial compounds have shown that the interstitial atoms occupy the 24d sites accompanied by an increase in the distance between the icosahedral clusters.[20] For $LaFe_{13-x}Al_x$ with x=2.0, the Fe–Fe distance is in the range where the exchange constant increases with increasing Fe–Fe distance. The Curie temperature of the rare-earth (R) transition metal (T) compounds depends on the magnitude of the exchange coupling between T–T atoms J_{TT}, the R–T coupling J_{RT} and the R–R coupling J_{RR}. In the $LaFe_{13-x}Al_x$ compounds, the R is nonmagnetic, and the relation between T_C and exchange interaction constant should be

$$3kT_C = 2Z_{TT}J_{TT}S_T(S_T+1).$$

Here Z_{TT} is the average nearest neighbouring T atoms, and k is the Boltzmann constant. S_T is the so-called pseudospin, which is related to the 3d magnetic moment M_T by

$$M_T = -g_T S_T \mu_B.$$

So the increase of J_{TT} due to the volume expansion associated with the carbon absorption leads to a significant increase of T_C. Figure 2 shows the thermomagnetization curves for all the samples under an applied field of 0.01T. The value of T_C is 200, 247 and 291K for x=0, 0.2 and 0.5, respectively. With increasing temperature, a drastic decrease in magnetization is observed at T_C, that is, the magnitude of $\partial M/\partial T$ around T_C remains very large, which is very important for the large magnetic entropy changes. A similar increase of T_C has also been found in the $La(Fe_xAl_{1-x})_{13}$ nitrides and hydrides.

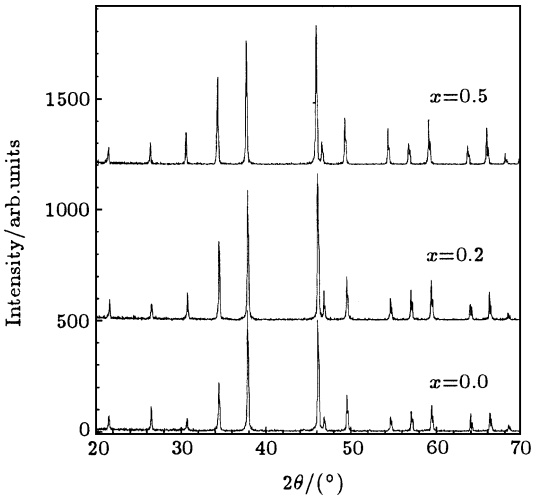


Fig.1. Powder XRD patterns for $LaFe_{11}Al_2C_x$ compounds.

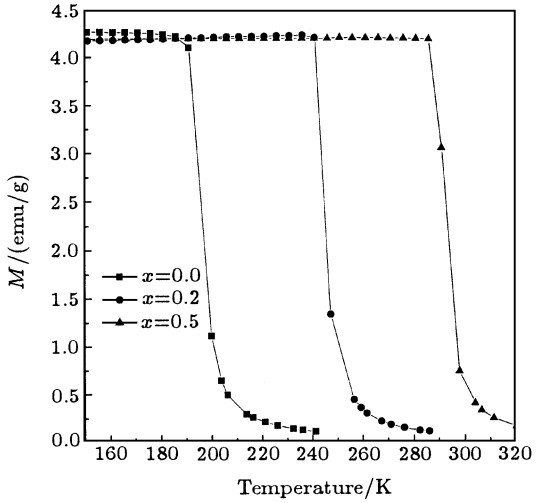


Fig.2. Temperature dependence of magnetization for $LaFe_{11}Al_2C_x$ compounds measured under a magnetic field of 0.01T.

Figure 3 shows the magnetization curves for the $LaFe_{11}Al_2C_x$ compounds at 5K. All the magnetization curves are easily saturated because the cubic $NaZn_{13}$-type structure has hardly any magnetocrystalline anisotropy due to the high crystallographic symmetry ($Fm3c$). The value of M_S at 5K is 1.81, 1.88 and 1.93 μ_B for x=0.0, 0.2 and 0.5, respectively, which increases slightly with the carbon concentration. It has been found that the interstitial atoms have two effects, i.e. the lattice expansion and the hybridization between the electronic orbitals of the interstitial and magnetic atoms, affecting the magnetic properties.[27] Introducing the carbon atoms will reduce the local band width, and this band narrowing thereby enhances the magnetic moment of Fe atoms.

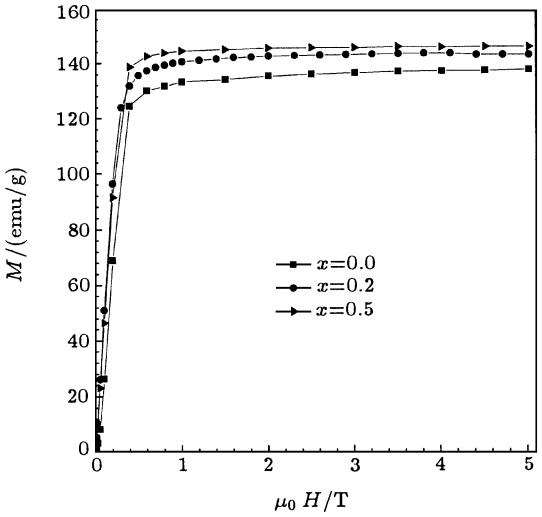


Fig.3. Magnetic field dependence of magnetization for $LaFe_{11}Al_2C_x$ compounds measured at 5K.

Figure 4 presents the isothermal magnetization for the samples with x=0.2 and x=0.5 at different temperatures in a wide temperature range. The sweep rate is slow enough to ensure M–H curves to be in isothermal equilibrium. The temperature step is 3K in the vicinity of T_C and 5K for the region far away from T_C. The M–H curves upon field increasing and decreasing show completely reversible behaviour, which is considered to be a very favourable characteristic for magnetic refrigeration applications.

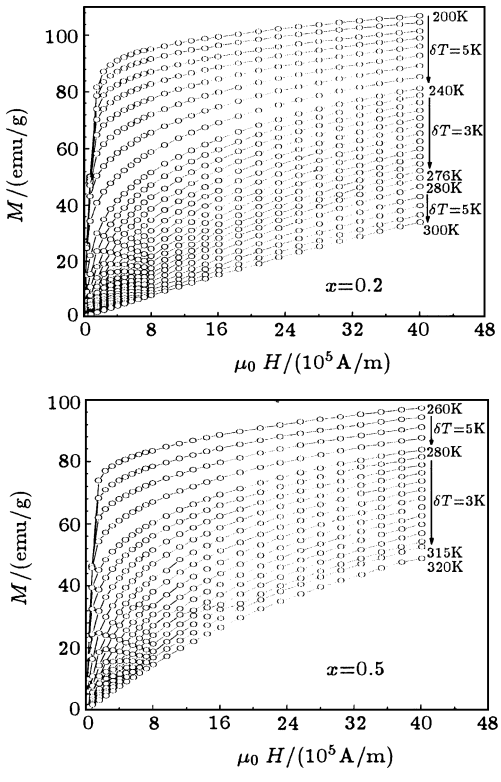


Fig.4. Isothermal magnetization of $LaFe_{11}Al_2C_{0.2}$ and $LaFe_{11}Al_2C_{0.5}$ at different temperatures.

The magnetic entropy change $|\Delta S|_m$ is calculated from the Maxwell relation

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

using the collected magnetization data. Figure 5 shows the magnetic entropy change of $LaFe_{11}Al_2C_x$ (x=0.2, 0.5) as a function of temperature under different magnetic fields. The maximum $|\Delta S|_m$ under an applied field of 5T is 6.1 and 6.3J/kg·K for x=0.2 (T_C ~247K) and x=0.5 (T_C ~ 291K), respectively. They are slightly smaller than that of Gd (9.7J/kg·K, T_C ~293K). The full width at half maximum, δT_{FWHM}, defined as the temperature interval corresponding to the half maximum of $|\Delta S|$,[28] is about 70K. This large magnetic entropy change in $LaFe_{11}Al_2C_x$ compounds is related to the high magnetization and the drastic decrease in the magnetization around T_C.

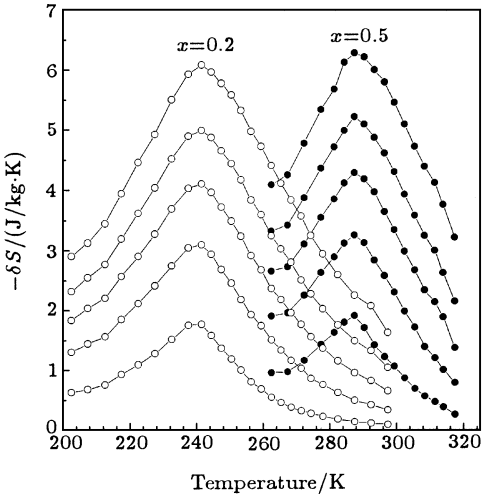


Fig.5. Temperature dependence of magnetic entropy change of $LaFe_{11}Al_2C_{0.2}$ and $LaFe_{11}Al_2C_{0.5}$ under the magnetic field changes of 0–2T and 0–5T.

From the molecular theory, we have at T_C

$$\Delta S_m \approx -1.07qR\left(\frac{g\mu_B JH}{kT_C}\right)^{2/3},$$

where q is the number of magnetic ions per mole, R is the gas constant and g is the Lande factor. That is the so-called $H^{2/3}$ power law for $|\Delta S|_m$.[29] Figure 5 displays the magnetic entropy change $|\Delta S|$ at T_C as a function of $H^{2/3}$. One can see that $|\Delta S|_m$ is indeed proportional to $H^{2/3}$, suggesting the well-localized Fe moment in $LaFe_{11}Al_2C_x$ compounds and the $|\Delta S|_m$ sensitive to the change of applied field.

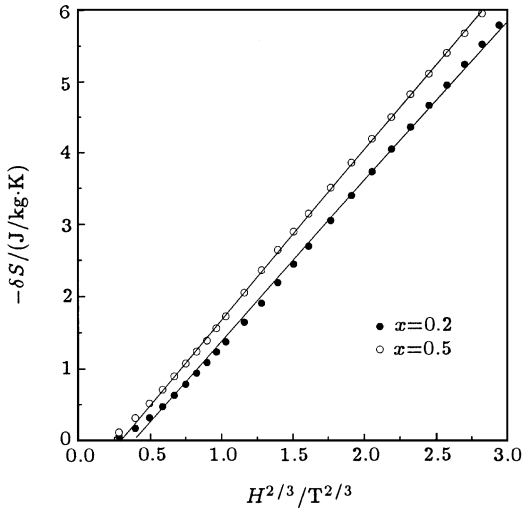


Fig.6. The magnetic entropy change $|\Delta S|$ at T_{C} as a function of $H^{2/3}$ for $LaFe_{11}Al_2C_{0.2}$ and $LaFe_{11}Al_2C_{0.5}$.

As can be seen from the above, T_{C} of the $LaFe_{11}Al_2C_x$ compounds can be tunable from 200K to room temperature by controlling the carbon concentration. And the value of M_{S} at 5K increases slightly with increasing carbon concentration by reducing the overlap of the Fe 3d wavefunctions. One can obtain a large magnetic entropy change in compounds of $LaFe_{11}Al_2C_x$ over a large temperature range, which is desired for the application to the Ericsson-type magnetic refrigerator. Furthermore, our compounds are much cheaper than materials reported previously due to the high content of Fe.

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