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Magnetocaloric effect in La$(Fe_{0.88}Al_{0.12})_{13}C_x$ interstitial compounds

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Abstract
The magnetocaloric effect and the order of magnetic transition in La$(Fe_{0.88}Al_{0.12})_{13}C_x$ interstitial compounds have been investigated by means of magnetic measurements and Mössbauer spectroscopy. With increasing carbon content from $x = 0.2$ to 0.6, the maximum magnetic entropy change decreases from 9.6 to 8.3 J kg^{-1} K^{-1} under an external field of 5 T, which is comparable with that of pure Gd metal. Analyses of magnetic measurements and Mössbauer results indicate there is a weakly first order magnetic transition between ferromagnetic and paramagnetic (F–P) states at T_C for $x = 0.2$. Increasing the carbon content drives the F–P transition towards second order, which is the main reason why the magnetic entropy change decreases with increasing carbon content.

1. Introduction

Recently, much attention has been paid to materials with the giant magnetocaloric effect (MCE) at room temperature due to their potential as room temperature magnetic refrigerants. Generally, due to their high magnetic moments, heavy rare earth elements and their compounds are considered to be the best candidate materials for finding a large MCE. Gd metal has the highest MCE involving a second order magnetic transition, which shows a maximum entropy change, ΔS, of 9.7 J kg^{-1} K^{-1} under a 5 T field at $T_C = 293$ K [1]. Pecharsky and Gschneidner [2] have discovered a giant MCE in $Gd_5Si_2Ge_2$ ($\Delta S = 18.5$ J kg^{-1} K^{-1} under a 5 T field at $T_C = 276$ K). The most important feature is that it undergoes a simultaneous first order structural and magnetic transition induced by temperature or/and an external magnetic field, which is responsible for the large magnetic entropy change near T_C. The change of the crystal structure takes place via a collective shear mode that is easily affected by the magnetic field, temperature and pressure [3, 4]. Much research has been conducted on $R_5(Si_xGe_{1-x})_4$ [2–12] and $R_5(Si_xSn_{1-x})_4$ [13–15] systems in order to find other giant MCE materials and understand the mechanism of the giant MCE. A temperature and external magnetic field induced first order magnetostructural transition is also reported in Gd_5Sn_4 [13]. A pressure and magnetic field induced first order magnetostructural phase transition has been found in Gd_5Ge_4 [9,10]. Er_5Si_4 shows a reversible first order structural transition without coupling with magnetic transition [11] and the compound possesses a canted magnetic structure below 32 K, according to the neutron diffraction results [16]. Very recently, it has been reported that the replacement of a small amount of Ge by Fe in $Gd_5Si_2Ge_2$ can substantially reduce the hysteresis loss during the magnetic field cycle [17]. Compared with $Gd_5Si_2Ge_2$, $Gd_5Si_2Ge_{1.9}Fe_{0.1}$ exhibits a broader ΔS peak. Although the addition of iron does not significantly affect the refrigerant capacity of the material, a greater net capacity is obtained for the iron containing alloy when the hysteresis loss is accounted for.

Large magnetic entropy changes are also observed in other systems. The lanthanum–manganese perovskite compounds $(La_{1-x}M_x)MnO_3$ where M = Li, Na, Ca, Sr, Ba and Y show a large MCE in the temperature range from 250 to 350 K [18–22]. Several of these phases such as $(La_{1-x}Ca_x)MnO_3$ compounds [18, 20] display a magnetic entropy change

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comparable with that of Gd but smaller than those observed in the $Gd_5(Si_xGe_{1-x})_4$ system. From the known magnetic/structural/electronic phase diagram of $(La_{1-x}Ca_x)MnO_3$ [23], it is known that these compounds exhibit a ferromagnetic insulator/ferromagnetic metal transition for $0.18 \leqslant x \leqslant 0.28$ or a ferromagnetic metal/paramagnetic insulator transition for $0.28 \leqslant x \leqslant 0.50$, which is the possible reason for the large MCE. The FeRh alloy displays a giant MCE between 296 and 316 K due to a magnetic and structural order–order transformation [24]. The MCE behaviour is sensitive to the processing history and is irreversible under the magnetic field change cycle. The Heusler compounds of Ni–Mn–Ga also display a large magnetic entropy due to an abrupt change in the magnetization near the martensite-to-austenite phase transition [25, 26]. The $MnFeP_{1-x}As_x$ system [27–29] exhibits a reversible giant magnetic entropy change comparable with that of $Gd_5Si_2Ge_2$ because of a first order magnetic transition near T_C. The operating temperature can be tuned from about 150 to about 335 K by adjusting the P/As ratio. The large entropy change is due to a field induced first order magnetic transition above T_C. The broad range of working temperature, the large MCE and the relatively low cost make them promising candidates as room temperature magnetic refrigerants.

$La(Fe_{1-x}Si_x)_{13}$ compounds with a cubic $NaZn_{13}$ structure display a high magnetization, and their Curie temperature is in the room temperature range from about 190 to 250 K [30]. In addition, $La(Fe_{1-x}Si_x)_{13}$ with a low Si content show an itinerant electron metamagnetic transition above T_C and a negative lattice expansion at T_C [31], which results in a sharp change in magnetization. Compounds based on $La(Fe_{1-x}Si_x)_{13}$ could be appropriate materials for exploring magnetic refrigerants for room temperature applications. $LaFe_{11.4}Si_{1.6}$ shows a maximum magnetic entropy change up to $19.4\ J\ kg^{-1}\ K^{-1}$ at $T_C = 208$ K under a magnetic field change of 5 T due to a first order magnetic transition at T_C [32]. The Curie temperature could be adjusted by substituting some Fe by other elements in $LaFe_{11.4}Si_{1.6}$. Increasing the Si content, x, from 1.6 to 2.6 enhances T_C from 208 to 248 K, but the magnetic entropy change decreases to $5.9\ J\ kg^{-1}\ K^{-1}$ under a magnetic field of 5 T at T_C in $LaFe_{13-x}Si_x$ compounds [33]. Mössbauer results indicate that the order of the paramagnetic-to-ferromagnetic phase transition (F–P) at T_C changes from first order to second order in $LaFe_{13-x}Si_x$ [34]. On the other hand, $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ compounds with $x = 0$–0.1 possess a T_C between about 200 and 300 K and display large magnetic entropy changes larger than or similar to that of Gd, and the order of magnetic transition changes from strong first order to weakly first order and second order [35, 36]. With increasing Mn content, T_C decreases from 188 to 127 K and ΔS decreases from 26.0 to $17.1\ J\ kg^{-1}\ K^{-1}$ in $La(Fe_{1-x}Mn_x)_{11.7}Si_{1.3}$ compounds [37]. T_C increases from 195 to 250 K and ΔS decreases from 24.8 to $12.1\ J\ kg^{-1}\ K^{-1}$ in $LaFe_{11.6}Si_{1.4}C_x$ interstitial compounds with x increasing from 0 to 0.6 [38]. However, α-Fe will appear and the 1 : 13 phase is difficult to form as x is larger than 0.4 in the interstitial compounds. The compound $La(Fe_{0.98}Co_{0.02})_{11.7}Al_{1.3}$ displays a large magnetic entropy change of $10.6\ J\ kg^{-1}\ K^{-1}$ under a field change of 5 T at its T_C of 198 K [39].

$La(Fe_xAl_{1-x})_{13}$ compounds with the cubic $NaZn_{13}$ structure have antiferromagnetic ground states along with a very sharp metamagnetic transition in external fields of a few teslas for $x \geqslant 0.86$ [40]. Hydrogenation of $La(Fe_{0.88}Al_{0.12})_{13}$ changes the magnetic ground state from the antiferromagnetic to the ferromagnetic state, while the hydride is not chemically stable [41]. Recently, we have found that insertion of interstitial C atoms into $La(Fe_{0.88}Al_{0.12})_{13}$ also changes the magnetic ground state from the antiferromagnetic to the ferromagnetic state, accompanied by a significant increase in T_C [42]. The carbides were prepared using the arc-melting technique and possess good chemical stability. In this paper, we report on the magnetic entropy change and the type of magnetic transition in $La(Fe_{0.88}Al_{0.12})_{13}C_x$ compounds.

2. Experimental techniques

Polycrystalline ingots of $La(Fe_{0.88}Al_{0.12})_{13}C_x$ ($x = 0$, 0.2, 0.4 and 0.6) were prepared in a purified Ar atmosphere using a tri-arc melting method. The ingots were annealed at 1173 K for 15 days in evacuated quartz tubes. X-ray powder diffraction analysis was performed in an automated Nicolet X-ray Powder Diffractometer with Cu K_α radiation. The Curie temperatures were determined from the ac susceptibility (χ_{ac}), using a quantum design physical property measurement system (PPMS) magnetometer. The magnetometer (PPMS) was also used for dc-magnetization measurements in fields of up to 9 T.

The Mössbauer spectra for $La(Fe_{0.88}Al_{0.12})_{13}C_x$ samples were obtained in a standard transmission geometry with a 1 GBq ^{57}CoRh source on a constant acceleration spectrometer, which was calibrated against an α-iron foil at room temperature. A liquid nitrogen flow cryostat was used to obtain temperatures between 100 and 300 K. Spectra were fitted using a standard nonlinear least-squares minimization method.

3. Results and discussion

3.1. Magnetic entropy change in $La(Fe_{0.88}Al_{0.12})_{13}C_x$ compounds

The x-ray diffraction (XRD) results indicate that all the alloys crystallized in a single phase with the $NaZn_{13}$ type cubic structure except for the presence of a few per cent of α-Fe in the alloy with $x = 0.6$. As expected, the addition of carbon changed the antiferromagnetic state to a ferromagnetic state. The magnetic transition temperature increased from 200 to 266 K for $x = 0$ to 0.6.

The magnetization for $La(Fe_{0.88}Al_{0.12})_{13}C_x$ was measured as a function of the applied magnetic field and temperature near T_C. The magnetic entropy change, ΔS, was calculated using Maxwell's thermodynamic relation. The accuracy of the calculated ΔS using this technique is about 3–10% [1]. The magnetic entropy change is given by

$$\Delta S(T, H) = \int_0^H \left(\frac{dM}{dT}\right) dH. \tag{1}$$

Figure 1 shows the temperature dependence of the magnetic entropy change, ΔS, for $La(Fe_{0.88}Al_{0.12})_{13}C_x$ with $x = 0.2$, 0.4 and 0.6 under different applied magnetic fields. The maximum magnetic entropy change, ΔS, ranges from about $9.6\ J\ kg^{-1}\ K^{-1}$ to $8.3\ J\ kg^{-1}\ K^{-1}$ under an external field change of 5 T, comparable with that of pure Gd metal

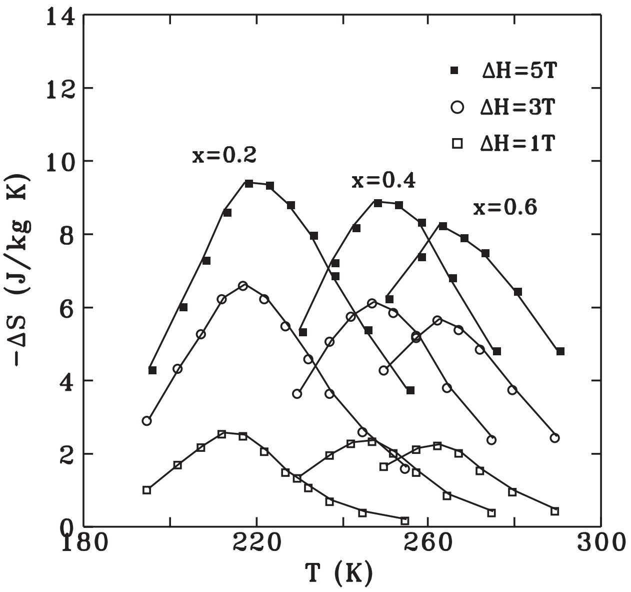

Figure 1. Temperature dependence of magnetic entropy change for La(Fe$_{0.88}$Al$_{0.12}$)$_{13}$C$_x$ under different magnetic fields.

(9.7 J kg^{-1} K^{-1}) [1]. With increasing external magnetic field, the ΔS peak for $x = 0.2$ broadens and shows a slight asymmetry. Further, the ΔS peak position shifts to a higher temperature with increasing applied field. This indicates the occurence of a field induced magnetic phase transition above T_C. However, the magnetic entropy change decreases with increasing carbon content. Further, the asymmetry of the ΔS peak for $x = 0.4$ is smaller and that for $x = 0.6$ disappears.

3.2. The order of magnetic transition in La(Fe$_{0.88}$Al$_{0.12}$)$_{13}$C$_x$

The temperature and field dependence of the magnetic free energy near the magnetic transition temperature determines the order of the transition. In Landau theory, expanded up to the M^6 term [43], the magnetic free energy, $F(M, T)$, and the corresponding state equation linking the magnetization, M, and the magnetic field, $\mu_0 H$, are respectively, given by

$$F(M,T) = \frac{a_1(T)}{2}M^2 + \frac{a_3(T)}{4}M^4 + \frac{a_5(T)}{6}M^6 + \cdots - \mu_0 HM, \qquad (2)$$

$$\mu_0 H = a_1(T)M + a_3(T)M^3 + a_5(T)M^5. \qquad (3)$$

The temperature dependence of the leading order Landau coefficients $a_1(T)$ and $a_3(T)$ allows us to identify two characteristic temperatures and thereby distinguish first and second order magnetic transitions. The susceptibility must be positive and exhibits a maximum at T_C, and therefore the (positive) minimum in $a_1(T)$ marks $T_C^{a_1}$. $a_3(T)$ crosses zero at a second temperature, T_0. In La(Fe$_{0.88}$Al$_{0.12}$)$_{13}$C$_x$ compounds, the magnetic contribution is from the 3d Fe magnetic subsystem and T_0 will be larger than or equal to T_C. If $T_0 = T_C$, then the transition is second order, while $T_0 > T_C$ implies a first order transition [43].

La(Fe$_{0.88}$Al$_{0.12}$)$_{13}$C$_x$ is magnetically soft with coercivities ($\mu_0 H_{ci}$) less than 2 mT, allowing the demagnetization factor to be determined from the initial slope of magnetization curves obtained below T_C. All magnetization data presented here have been corrected using a demagnetizing factor of about 0.12.

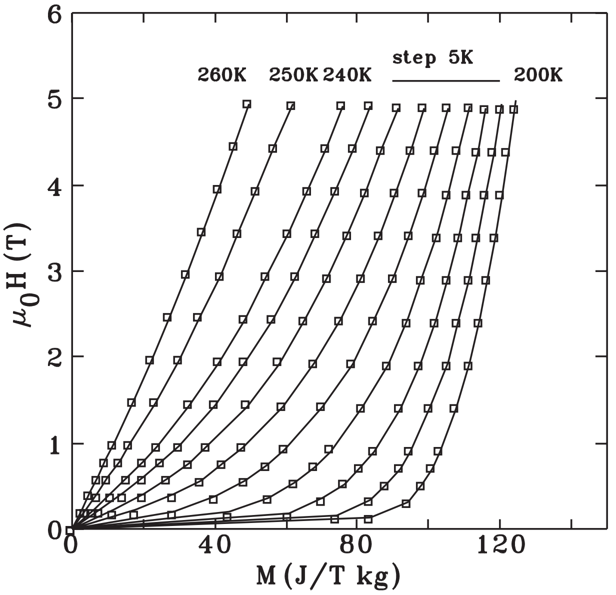

Figure 2. Magnetization, $M(\mu_0 H)$, of La(Fe$_{0.88}$Al$_{0.12}$)$_{13}$C$_{0.2}$ at different temperatures. The solid lines represent the fits to equation (3).

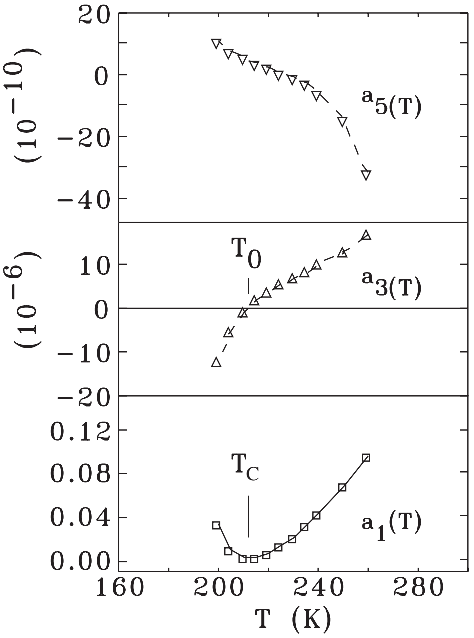

Figure 3. Temperature dependence of Landau coefficients for La(Fe$_{0.88}$Al$_{0.12}$)$_{13}$C$_{0.2}$ compound. The units for $a_1(T)$, $a_3(T)$ and $a_5(T)$ are T^2 kg J^{-1}, T^4 kg^3 J^{-3} and T^6 kg^5 J^{-5}, respectively. Error bars are smaller than the points.

The Landau coefficients $a_1(T)$, $a_3(T)$ and $a_5(T)$ were determined by fitting the magnetic field, $\mu_0 H$, against magnetization, $M(\mu_0 H)$, using equation (3). As an example, figure 2 shows magnetization data for La(Fe$_{0.88}$Al$_{0.12}$)$_{13}$C$_x$ with $x = 0.2$ at different temperatures together with the fitted curves. The temperature dependence of the Landau coefficients derived from these fits for $x = 0.2$ is shown in figure 3.

Table 1. Characteristic temperatures for $La(Fe_{0.88}Al_{0.12})_{13}C_x$ compounds.

x	T_C^{χ} (susceptibility) (K)	$T_C^{B_{hf}}$ (Mössbauer) (K)	T_C^{Br} (Brillouin) (K)	$T_C^{a_1}$ ($a_1(T)$ in min)	T_0 ($a_3(T) = 0$) (K)
0.2	217 ± 1	220 ± 3	250 ± 5	216 ± 3	218 ± 3
0.4	247 ± 1			245 ± 3	245 ± 3
0.6	266 ± 1	265 ± 3	265 ± 4	265 ± 3	265 ± 3

As expected, $a_1(T)$ is positive with a minimum at T_C, corresponding to a maximum in the susceptibility, χ, for all compounds. Similarly, $a_3(T)$ increases from negative to positive, crossing zero at T_0. The derived $T_C^{a_1}$, T_0 and Curie temperature, T_C^{ac}, determined using the ac susceptibility method are listed in table 1. The derived $T_C^{a_1}$ is, within error, the same as the magnetic transition temperature, T_C^{ac}. T_0, within error, is equal to $T_C^{a_1}$ for all compounds, indicating that the zero external field magnetic transition at T_C should be a second order one or a very weakly first order.

As stated above, the ΔS–T relation for $x = 0.2$ (figure 1) shows clearly the occurrence of a field induced first order magnetic transition. In order to gain more insight into the nature of the magnetic transition in $La(Fe_{0.88}Al_{0.12})_{13}C_x$ alloys, Mössbauer spectra were obtained at different temperatures.

As shown in figure 4(*a*), the ^{57}Fe Mössbauer spectrum for $x = 0.2$ is obtained with increasing temperature from 100 to 295 K. The spectrum for $x = 0.2$ is dominated by a magnetic sextet with a Voigt lineshape (i.e. a Gaussian distribution of Lorentzian lines) at temperatures below 215 K. With increasing temperature, the average hyperfine field, $B_{hf}(T)$, of the sextet decreases (figure 4(*a*)). However, in addition to the sextet corresponding to a magnetically ordered state, there is an asymmetric doublet indicating a paramagnetic state between 220 and 230 K. At 235 K, the average hyperfine field, B_{hf}, decreases to zero and the sextet component is replaced by a doublet indicating the paramagnetic state of the compound.

The temperature dependent Mössbauer spectra for $x = 0.6$ are shown in figure 5(*a*). The spectra have a very small subspectrum corresponding to α-Fe (<5 at.%) and are in agreement with the XRD results. The average hyperfine field, B_{hf}, decreases gradually to zero with increasing temperature from 100 to 265 K (figure 5(*b*)). An asymmetric doublet appears and completely replaces the magnetic sextet at 265 K. There is no sign of the coexistence of the magnetic sextet and paramagnetic doublet for $x = 0.6$.

There is an approximately linear correlation between the mean hyperfine field, $B_{hf}(T)$, and the mean magnetic moment. The temperature dependence of $M(T)$ can be determined by solving the equation $M(T) = M(0)B_J((M(T)/M(0))/(T/T_C))$ based on a mean field theory for $T \leqslant T_C$, where the function $B_J(x) = ((2J + 1)/2J)\coth((2J + 1)x/2J) - (1/2J)\coth(x/2J)$ is the Brillouin function (BF) and the calculated $M(T)$ is referred to as a BF relation [44]. The mean field theory predicts the magnetic transition at T_C to be second order. If the temperature dependence of $M(T)$ obviously deviates from the BF relation near T_C, the magnetic transition should be first order. $B_{hf}(T)$ could be thus expressed by a BF with $J = \frac{1}{2}$, as

$$B_{hf}(T) = B_{hf}(0)B_{1/2}(x), \tag{4}$$

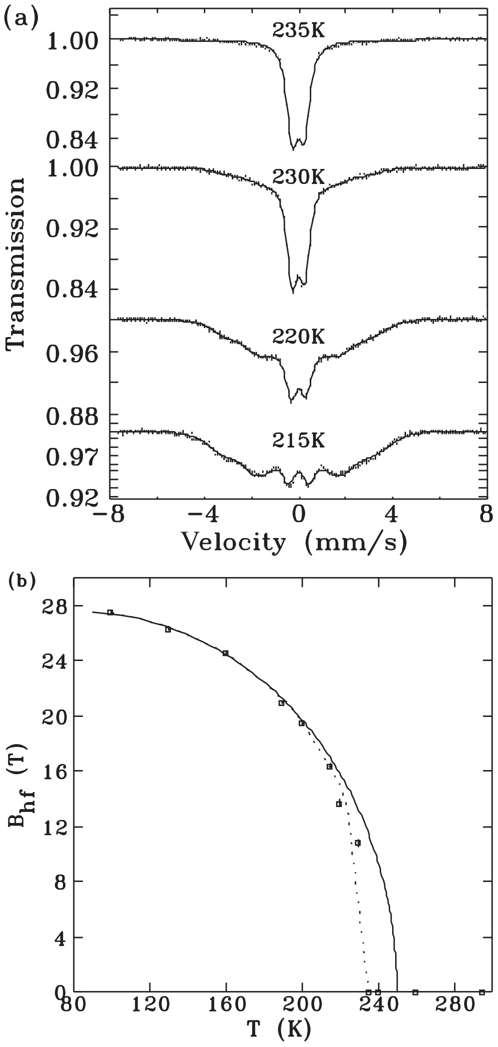

Figure 4. (*a*) ^{57}Fe Mössbauer spectra of $La(Fe_{0.88}Al_{0.12})_{13}C_{0.2}$ with increasing temperature. The solid lines are least-square fits to the Mössbauer spectra. (*b*) Temperature dependence of the average hyperfine magnetic field. The solid line is calculated using equation (4). The dashed line through the experimental data points is only a guide for the eye.

where

$$B_{1/2}(x) = 2\coth(2x) - \coth(x), \qquad x = \frac{b_{hf}}{t}, \quad t = \frac{T}{T_C}.$$

$B_{hf}(T)$ for $La(Fe_{0.88}Al_{0.12})_{13}C_x$ compounds was fitted using a standard least-squares method and equation (4). The details of the fitting method have been given elsewhere [34]. As shown in figure 4(*b*), with increasing temperature, $B_{hf}(T)$ for $x = 0.2$ changes more sharply than that predicted by the BF relation near T_C. The result indicates a first order magnetic

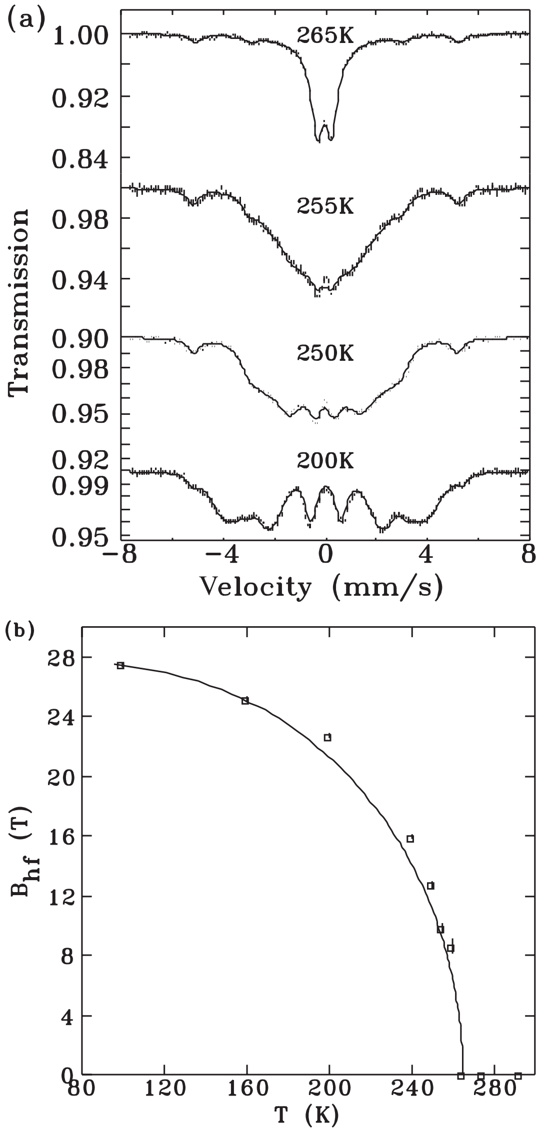

Figure 5. (*a*) ^{57}Fe Mössbauer spectra of $La(Fe_{0.88}Al_{0.12})_{13}C_{0.6}$ with increasing temperature. The solid lines are least-square fits to the Mössbauer spectra. (*b*) Temperature dependence of the average hyperfine magnetic field. The solid line is calculated using equation (4).

phase transition has taken place at T_C under zero external field. The coexistence of FM and PM states may be due to the hysteretic effect of the first order magnetic transition around T_C, although another possibility that cannot be discounted is the effect of the composition heterogeneity in the sample, leading to a distribution in local ordering temperatures (figure 4(*a*)). On the other hand, $B_{hf}(T)$ for $x = 0.6$ can be fitted very well using a BF relation, indicating the occurrence of a second order magnetic transition at T_C.

The fitted T_C^{Br} values are listed in table 1 together with the $T_C^{B_{hf}}$ values determined from the point at which the paramagnetic doublet appears in the Mössbauer spectra. The transition temperatures, T_C^{χ}, obtained from χ_{ac} measurements, are identical within error to $T_C^{B_{hf}}$. For $x = 0.6$, $T_C^{B_{hf}}$ is the same as T_C^{Br} because the temperature dependence of $B_{hf}(T)$ can be well fitted by the BF relation. However, $B_{hf}(T)$ for $x = 0.2$ changes more sharply than predicted by the BF relation near T_C and so $T_C^{B_{hf}}$ is smaller than T_C^{Br}.

From the magnetic measurements (figure 1 and table 1) and Mössbauer results, there should be a weakly first order, a very weakly first order and a second order magnetic transition at T_C for $x = 0.2$, 0.4 and 0.6, respectively.

4. Conclusions

The ferromagnetic interstitial compounds $La(Fe_{0.88}Al_{0.12})_{13}C_x$ with the cubic $NaZn_{13}$ structure exhibit a large magnetic entropy of 8.2–9.6 $J\,kg^{-1}\,K^{-1}$, comparable with that of pure Gd metal near their T_C under an external field change of 5 T. The temperature dependence of the Landau coefficients and Mössbauer results indicate that a weakly first order and a second order magnetic transition has taken place for the compounds with $x = 0.2$ and $x = 0.6$, respectively. The large entropy change and the low material cost make these interstitial compounds promising for use as magnetic refrigerants in a temperature range from 200 to 300 K.

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