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2004 J. Phys.: Condens. Matter 16 2103

(http://iopscience.iop.org/0953-8984/16/12/019)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) 2103–2108 PII: S0953-8984(04)72662-4

The large magnetic entropy change and the change in the magnetic ground state of the antiferromagnetic compound $LaFe_{11.5}Al_{1.5}$ caused by carbonization

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Received 26 November 2003
Published 12 March 2004
Online at stacks.iop.org/JPhysCM/16/2103 (DOI: 10.1088/0953-8984/16/12/019)

Abstract

The large magnetic entropy change and changes in the magnetic properties of the antiferromagnetic compound $LaFe_{11.5}Al_{1.5}$ caused by carbonization have been investigated. Both the parent compound $LaFe_{11.5}Al_{1.5}$ and its carbides crystallize in the cubic $NaZn_{13}$-type structure. Carbonization brings about an obvious increase in the lattice parameter. The magnetic ground state is changed from an antiferromagnetic to a ferromagnetic one by carbonization. A considerable increase of Curie temperature, varying from 191 to 262 K with carbon concentration increasing from 0.1 to 0.5, is observed due to the decrease in the overlap of the Fe 3d wavefunctions caused by the volume expansion. Meanwhile, only a slight increase of the saturation magnetization is found as compared with the variation in Curie temperature. All the $LaFe_{11.5}Al_{1.5}$ carbides exhibit a considerable magnetic entropy change, comparable with that in Gd around the Curie temperature. Thus, one can get a large magnetic entropy change over a wide temperature range by controlling the carbon concentration. This large magnetic entropy change can be attributed to the high magnetization and a sharp drop in magnetization with increasing temperature near the Curie temperature.

1. Introduction

Magnetic refrigeration (MR) research has attracted much attention since the magnetocaloric effect (MCE) was first observed in iron in 1881, due to its potential applications in producing higher efficiency and a lower environmental impact in comparison with conventional gas refrigeration [1]. The isothermal magnetic entropy change ΔS_m is a necessary value for evaluating the refrigerant properties [2]. So materials displaying large magnetic entropy changes at the temperature of interest are very important in MR technology [3–9]. Many

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attempts have been made to find materials with large magnetic entropy changes in the temperature range around room temperature. Rare earth Gd has been considered historically to be the best room temperature refrigerant because of its ideal Curie temperature T_C (293 K) and its large magnetic entropy change ($|\Delta S| \sim 9.8\,\mathrm{J\,kg^{-1}\,K^{-1}}$ under a magnetic field change from 0 to 5 T at T_C) [10]. However, the high price of Gd limits its wide application. It is important to find low cost materials displaying large magnetic entropy change around room temperature.

There are two prerequisites for a material to exhibit a large magnetic entropy change. One is a large spontaneous magnetization and the other is a sharp drop in the magnetization with increasing temperature around T_C. In rare earth intermetallic compounds formed with the 3d transition metals, the strong magnetic coupling gives rise to a high magnetization. $NaZn_{13}$-type structure $La(Fe, M)_{13}$ (M = Al, Si) has the largest Fe content among rare earth intermetallic compounds. Furthermore, due to the direct magnetic exchange interaction between Fe atoms, the magnetizations change relatively sharply in the vicinity of T_C as compared to those of rare earth based compounds. And correspondingly, a large magnetic entropy change has been found in the $NaZn_{13}$-type structure compounds $LaFe_{13-x}Si_x$ and $LaFe_{13-x}Al_x$ [11–14]. However, the large magnetic entropy change concentrates in a narrow temperature range below 200 K, which limits its application. Many efforts have been devoted to increasing the Curie temperature by substituting Co for Fe or by introducing interstitial atoms [15–17]. Nitrogenation and hydrogenation of $La(Fe_{1-x}Al_x)_{13}$ compounds have been carried out and the results show that the magnetic properties of $La(Fe_{1-x}Al_x)_{13}$ compounds are sensitive to volume change [18, 19].

In the present work, we choose the antiferromagnetic compound $LaFe_{11.5}Al_{1.5}$ as the parent compound and study the large magnetic entropy change and change in its ground magnetic state caused by introducing carbon atoms into it.

2. Experimental procedure

$LaFe_{11.5}Al_{1.5}C_x$ ($x = 0$–0.5) compounds were prepared by arc melting under a high purity argon atmosphere from starting materials with at least 3N purity, followed by annealing for two weeks at 900 °C. X-ray diffraction (XRD) measurements on powder samples using Cu Kα radiation were performed to identify the single phase and to determine the crystallographic structure. Magnetic measurements were performed on a commercial MPMS-7 superconducting quantum interference device (SQUID) magnetometer.

3. Results and discussion

Step-scan powder XRD measurements were performed on $LaFe_{11.5}Al_{1.5}C_x$ compounds at room temperature. The refinement by a Rietveld profile-fitting technique shows that the cubic $NaZn_{13}$-type structure ($Fm3c$) remains, but there is an obvious increase in lattice parameter upon carbonization. Our results confirm what has been observed in nitrides and hydrides of $La(Fe_{1-x}Al_x)_{13}$ compounds: that the interstitial carbon atoms occupy the interstitial site 24d [19, 20]. The lattice parameter increases monotonically from 11.5803 to 11.6356 Å and the volume expansion is about 1.5% with x varying from 0 to 0.5 as shown in figure 1. The interstitial atoms will produce two effects: lattice expansion and hybridization between the electronic orbitals of interstitial and magnetic atoms. The lattice expansion will result in the 3d band narrowing due to the decrease in overlap of the Fe 3d wavefunctions, thus leading to increase of T_C and the saturated magnetic moment μ_S. The hybridization will bring about the opposite effects on T_C and μ_S [21, 22, 19].

In the compound $LaFe_{13-x}Al_x$, La and Fe_I atoms form the CsCl-type structure. Fe_I atoms are each surrounded by an icosahedron of $12Fe_{II}$ atoms and possess a local symmetry peculiar to an FCC-like lattice. Such a peculiar local environment leads to antiferromagnetic

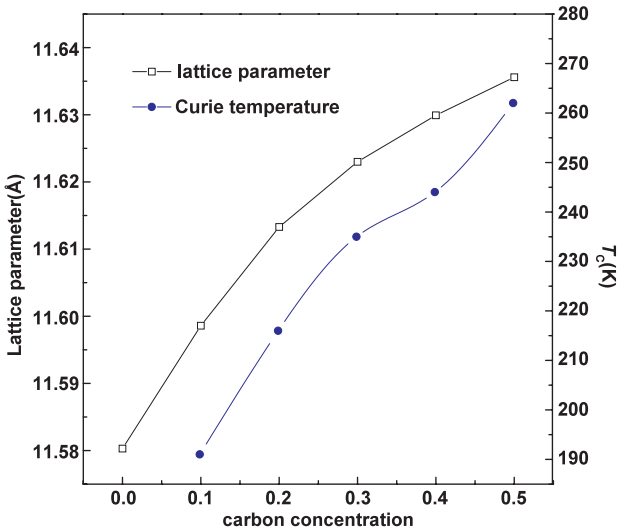

Figure 1. The carbon concentration dependence of the lattice parameter a and the Curie temperature T_C.

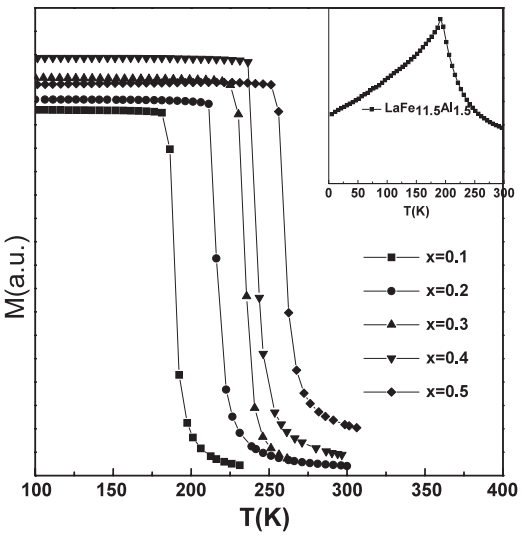

Figure 2. Thermomagnetic curves as a function of temperature measured under the low magnetic field of 0.01 T.

coupling between Fe atoms for high iron content. The changes in the lattice parameter and the coordination number can bring about a change in the magnetic ground state [23].

The thermomagnetic curves measured under a low magnetic field of 0.01 T are displayed in figure 2. One can see that, upon heating, the parent compound $LaFe_{11.5}Al_{1.5}$ undergoes a transition from an antiferromagnet to a paramagnet at the Néel temperature T_N 190 K. However, a ferromagnetic-to-paramagnetic transition is observed in all carbides at the respective T_C, which increases monotonically from 191 to 262 K with x varying from 0.1 to 0.5, as shown in figure 1. This suggests that the magnetic ground state of the compound $LaFe_{11.5}Al_{1.5}$ changes from antiferromagnetic to ferromagnetic upon carbonization.

The isothermal magnetization curves measured at 5 K, as shown in figure 3, also confirm the above conclusion. The magnetization increases slowly with increasing field until at a moderate critical field 3.2 T, a sharp metamagnetic antiferromagnetic-to-ferromagnetic transition is observed for the parent compound $LaFe_{11.5}Al_{1.5}$. A large hysteresis occurs in field increase

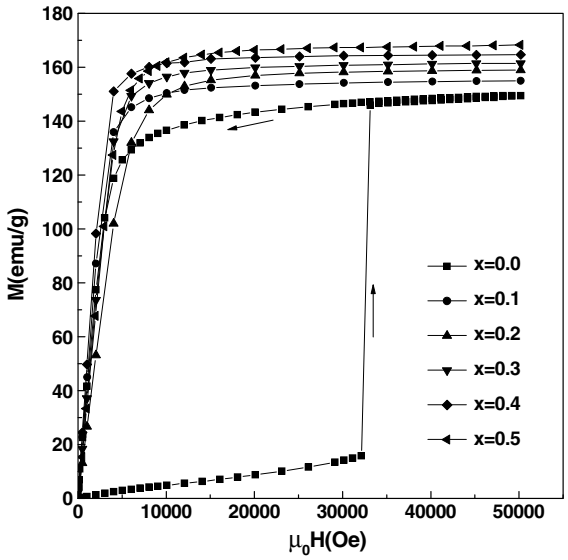

Figure 3. The magnetization curves measured at 5 K for the compounds $LaFe_{11.5}Al_{1.5}C_x$.

and decrease modes. A typical soft ferromagnetic state is found in all the carbides, however. This soft character is due to their special crystal structure. They all crystallize in the cubic $NaZn_{13}$-type structure with the $Fm3c$ space group. This has high space symmetry and very small anisotropy. One can also see that the saturated magnetic moment is high and increases slightly with increasing carbon concentration. This is also due to the lattice expansion. The carbon content dependences of T_C and μ_S can be fitted by the following linear equations:

$$T_C = 178.6 + 170x \tag{1}$$

$$\mu_S = 152 + 32.3x \tag{2}$$

where x is the carbon content. The slope of equation (1) is much larger than that of equation (2), which suggests that the change of the saturated magnetization with carbon concentration is much smaller than the significant increase of T_C.

From the above results one can see that the effects of carbon atoms on magnetic properties of $LaFe_{13-x}Al_x$ carbides are mainly caused by 3d band narrowing due to the decrease in the overlap of the Fe 3d wavefunctions accompanied by the expansion of the lattice parameter, while the hybridization between the electronic orbitals of interstitial and magnetic atoms plays a minor role. The larger the lattice parameter, the higher the Curie temperature and the saturation magnetization, which suggests that the magnetic properties of the compound $LaFe_{11.5}Al_{1.5}$ are sensitive to the volume change.

A sharp drop in the magnetization with increasing temperature around T_C is also found in the thermomagnetic curves; that is, the magnitude of $\partial M/\partial T$ around T_C remains very large. This characteristic is a very important parameter for materials displaying large magnetic entropy changes.

The magnetization isotherms for some of the carbides were measured in field increase mode over a wide temperature range. The sweep rate of the field is slow enough to ensure that M–H curves are in isothermal equilibrium. The temperature step is 3 K in the vicinity of T_C and 5 K for the range far away from T_C. Both field increase and decrease magnetizations are measured around T_C. Figure 4 shows the magnetic isotherms for the sample with $x = 0.4$ as an example. It is reversible upon field increase and decrease, which is very advantageous in practical MR application.

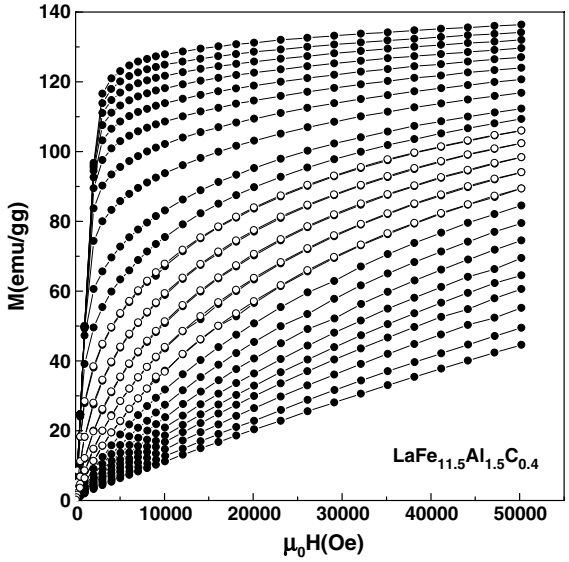

Figure 4. The magnetic isotherms for the compound $LaFe_{11.5}Al_{1.5}C_{0.4}$ over a wide temperature range from 190 to 280 K. The temperature step is 3 K between 242 and 266 K and 5 K for the other temperature ranges.

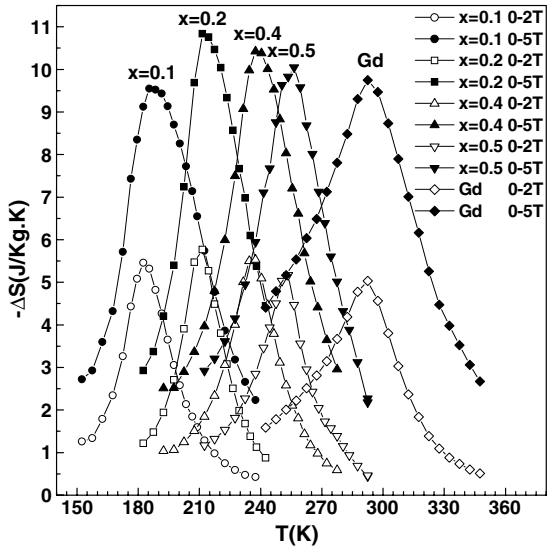

Figure 5. The temperature dependence of the magnetic entropy change $|\Delta S|_{\mathrm{mag}}$ under different magnetic field changes: 0–2 T (the hollow symbols) and 0–5 T (the solid symbols) for $LaFe_{11.5}Al_{1.5}C_x$ compounds and rare earth Gd as a comparison.

The values of the magnetic entropy change are obtained from Maxwell's relation $\Delta S(T, H) = -\int (\partial M/\partial T)_H \, \mathrm{d}H$ using collected magnetization data [24]. The magnetic entropy change as a function of temperature for the carbides under the different magnetic field changes of 0–2 and 0–5 T are shown in figure 5. One can see that all the carbides exhibit almost the same large value of magnetic entropy change around the respective Curie temperature. The peak value of $|\Delta S|$ is about 5.5, 5.8, 5.5 and 5.2 J kg^{-1} K^{-1} under a magnetic field change

from 0 to 2 T and 9.6, 10.8, 10.4 and 10.1 J kg^{-1} K^{-1} under a magnetic field change from 0 to 5 T for $x = 0.1$, 0.2, 0.4 and 0.5, respectively, almost comparable with or even larger than those for Gd ($|\Delta S| \sim 9.8$ J kg^{-1} K^{-1} under $\Delta H = 5$ T and $|\Delta S| \sim 4.5$ J kg^{-1} K^{-1} under $\Delta H = 2$ T; $T_C = 293$ K). In $LaFe_{13-x}Al_x$ compounds the strong magnetic coupling gives rise to a high magnetization. Carbon atoms have little effect on the saturated magnetic moment and they all exhibit a sharp change in magnetization around T_C due to the direct magnetic exchange interaction between Fe atoms. Maxwell's relation indicates that all the carbides should exhibit large magnetic entropy changes.

4. Conclusions

$LaFe_{11.5}Al_{1.5}C_x$ ($x = 0$–0.5) compounds are prepared and investigated. The magnetic ground state is changed from an antiferromagnetic to a ferromagnetic one by carbonization. The Curie temperature increases significantly from 191 to 262 K with x varying from 0.1 to 0.5, while the saturated magnetization increases only slightly as compared with the Curie temperature. A large magnetic entropy change commensurate with that of Gd is obtained for all the carbides. The large saturated magnetization due to the high content of iron and the sharp change of magnetization around the Curie temperature are the reasons of the large magnetic entropy change. Furthermore, it is almost field and temperature reversible, which makes the carbides promising magnetic refrigerants for the given temperature range.

Acknowledgments

This work was supported by the State Key Programme of Basic Research and the National Natural Science Foundation of China.

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