Magnetic phase in $LaFe_{11.4}Al_{1.6}$ with very low interstitial carbon content

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(Received 19 June 2006; revised manuscript received 16 August 2006; published 20 December 2006)

$NaZn_{13}$-type $LaFe_{11.4}Al_{1.6}C_\delta$ (δ=0–0.08) compounds were prepared by arc melting. At low temperature, the ground state is antiferromagnetic and ferromagnetic for δ=0 and 0.04, respectively. Although the ground state remains antiferromagnetic for δ=0.02, the ferromagnetic state can be induced by a magnetic field at about 100 K. During the transition between antiferromagnetic and ferromagnetic states, the magnetization exhibits a sharp discontinuity, indicating the formation of a homogeneous phase by intersitial carbon in spite of the very small δ. The transition from low-temperature antiferromagnetic state (AFI) to ferromagnetic state induced by a magnetic field is irreversible. On the contrary, the transition from high-temperature antiferromagnetic state (AFII) to ferromagnetic state is reversible. Considering the magnetization behaviors and the variation of heat capacity with temperature, we can deduce that the AFI is different from the AFII.

DOI: 10.1103/PhysRevB.74.212408 PACS number(s): 75.30Kz, 75.30Sg

I. INTRODUCTION

Since a large magnetic entropy change near room temperature was found in $Gd_5(Si,Ge)_4$ compounds in 1997,[1] the materials with first-order magnetic phase transition have attracted much attention due to their potential application as magnetic refrigerants (see Ref. 2 and the literatures therein). Among the materials showing large magnetocaloric effect (MCE), the cubic $NaZn_{13}$-type $La(Fe,Z)_{13}$ (Z=Si or Al) compounds are attracting a renewed interest.[3–10] Binary $LaFe_{13}$ does not exist. However the cubic phase can be formed by the partial substitution of Z for Fe. Itinerant-electron magnetism is the characteristic of $La(Fe,Z)_{13}$. For a small concentration of Z, there is an itinerant-electron metamagnetic transition (IEMT), i.e., the magnetic-field-induced first-order transition initially predicted by Wohlfarth and Rhodes from the Stoner model.[11] It is the IEMT that leads to large MCE.[5–7] Meanwhile, a remarkable magnetovolume effect (MVE) that keeps the structure unchanged is observed during IEMT in $La(Fe,Z)_{13}$ compounds.[3,8,9] However, large MCE is accompanied by a transition from monoclinic to orthorhombic structure and from hexagonal to orthorhombic structure for $Gd_5Si_2Ge_2$ and MnAs, respectively.[1,12,13]

Intensive investigation on macrophysical properties, such as the dependence of the transition on the Fe concentration, magnetic field, temperature and pressure, has been aroused due to both the large MCE and the remarkable MVE found in $La(Fe,Z)_{13}$ compounds. The low Curie temperatures, which limit the potential applications at room temperature, can be elevated either by the substitution of Co for Fe or by the interstitial effect of H, N, and C.[6,14–18] On the other hand, the theoretical model of IEMT, including the spin fluctuation effect, is setting up a clear connection between the band structure and the free energy (i.e., macrophysical properties).[19,20] The electronic structures of $La(Fe,Z)_{13}$ compounds have been used to discuss MVE.[9] However, the exploration of microphysical origin of IEMT is far from its final ending. One of the key problems is that the figure of antiferromagnetic (AF) state is not clear for $La(Fe,Al)_{13}$ with low Al content. In a $NaZn_{13}$-typed structure, 96(i) sites are occupied by 12 FeII+Al atoms and the centered 8(b) site is only occupied by 1 FeI atom.[4] Due to the symmetry of the crystal structure, it is impossible to obtain a simple antiferromagnetic lattice. With the help of neutron scattering and Mössbauer spectroscopy, a possible model of AF state was suggested.[4] That is, ferromagnetic (FM) clusters composed of 12 FeII+Al plus FeI are ferromagnetically coupled in (100) plane and the interplane coupling is AF. Because the Fe-Fe distance within a cluster is equal to that between the clusters, it is difficult to understand the different characteristics of the exchange coupling. Furthermore, after the lattice constant is enlarged by the introduction of interstitial atoms, such as H, N, and C, the magnetic ground state is changed from AF to FM state,[16–18] due to the sensitive dependence of exchange coupling on interatomic distance. However, for Z=Si, FM state is observed despite the Fe-Fe distance for Z=Si being smaller than that for Z=Al. Therefore, much attention should be paid to the characterization of the AF ground state for Z=Al.

Although both $LaFe_{11.5}Al_{1.5}$ and $LaFe_{11.44}Al_{1.56}$ compounds show AF ground states, $LaFe_{11.5}Al_{1.5}C_{0.1}$[18] and $LaFe_{11.44}Al_{1.56}C_{0.2}$[21] compounds have FM ground states. In other words, a small concentration of interstitial carbon definitely changes the magnetic ground state. In the present work, AF state and IEMT have been studied intensively for LaFeAl with a very low interstitial atom content. Carbon is chosen as the interstitial atom because its content can be easily controlled by direct arc melting using Fe-C alloy compared with that for H and N by gas-solid reaction.[16–18]

II. EXPERIMENT

Interstitial compounds $LaFe_{11.4}Al_{1.6}C_\delta$ (δ=0.0, 0.02, 0.04, 0.06, and 0.08) were prepared by arc melting an Fe-C alloy with La, Fe, and Al. The ingots were vacuum annealed for 13 days at 1223 K. A nearly single $NaZn_{13}$-type phase in the samples was confirmed by the results of x-ray diffraction (XRD). Magnetic measurements were performed on a com-

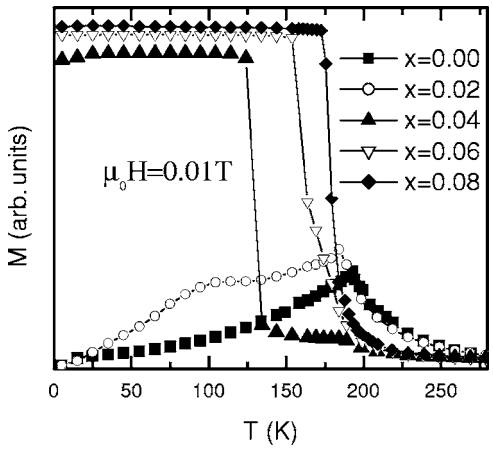

FIG. 1. The temperature dependence of magnetization under the field of 0.01 T measured in a zero-field-cooling (ZFC) process for $LaFe_{11.4}Al_{1.6}C_{\delta}$ (δ=0.0, 0.02, 0.04, 0.06, and 0.08) compounds.

mercial MPMS-7 (Quantum Design) superconducting quantum interference device magnetometer. The initial magnetization curve obtained after a zero-field-cooling (ZFC) process and then increasing from 0 to 5 T is termed the virgin curve, and those in the subsequent field cycling between 0 and 5 T are labeled as the ascending- and the descending-field curves. The specific heat was studied in a physical property measurement system (PPMS, Quantum Design) using the relaxation time method.

III. RESULTS AND DISCUSSION

Figure 1 shows the ZFC temperature dependence of magnetization under the field of 0.01 T. The compound without interstitial C undergoes an AF-to-PM transition, and the Néel temperature indicated by the cusp as shown in the figure is 193 K, which is well consistent with that reported in Refs. 3 and 22. As δ increases, the low-temperature ground state changes from AF to FM states. For δ=0.08, FM-to-AF transition temperature increases up to the Néel temperature. As reported in Refs. 16–18, the interstitial atom H, N, or C occupies 24d site in $NaZn_{13}$ structure, and the concentration of interstitial atom is 3 per formula unit. So, it is interesting that the magnetic ground state can be changed from AF to FM by 1 carbon atom in averaged 25 formula units for the samples with δ=0.04. Although the concentration of Al in the parent compound (i.e., δ=0.0) is near the critical for FM state, the magnetic exchange interactions are exceptionally sensitive to the carbon content. Further research into the effect of interstitial atom on the magnetic properties is needed.

There is an abnormal variation of magnetization at temperature around 100 K for δ=0.02 as shown in Fig. 1. Here, we focus on the magnetic properties of the compound with δ=0.02. Figure 2 shows the ZFC temperature dependence of magnetization at some typical fields for δ=0.02. Under the field of 0.35 T, the variation of magnetization with temperature is similar to that obtained at $\mu_0 H$=0.01 T (as shown in Fig. 1) where no obvious FM state is observed. FM state is induced around 100 K under the field of 0.36 T. For convenience, AFI is defined as the AF state at the low temperature,

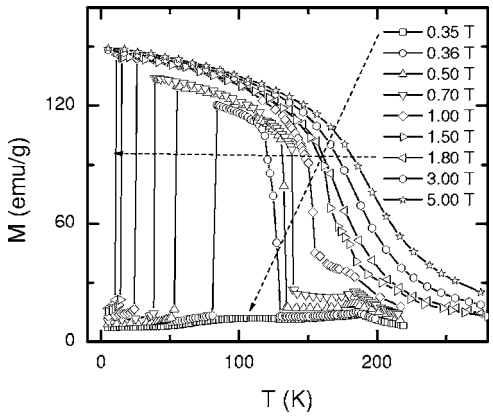

FIG. 2. The ZFC temperature dependence of magnetization at some typical field for δ=0.02.

and AFII is that at the high temperature. Thus, under the field of 0.36 T, the AFI-to-FM transition temperature T_{C1} and the FM-to-AFII transition temperature T_{C2} are about 82 and 127 K, respectively. Further increasing the field, T_{C1} decreases and T_{C2} increases as shown in Fig. 2. FM state, instead of AFI, is observed at the field of 2.50 T. FM-to-PM instead of AFII-to-PM transition is observed at the field of 1.80 T. Additionally, a sharp AFI-to-FM or FM-to-AFII change of magnetization indicates a homogeneous modification of magnetic state by the very low interstitial C content.

When the temperature dependence of magnetization is measured in a field-cooling (FC) process, AFI is replaced by FM state as long as $\mu_0 H \geq 0.36$ T. On the contrary, T_{C2} remains unchanged in the FC process. The FC and ZFC magnetic phase diagrams are shown in Fig. 3. The relationship between T_{C1} and H is largely different from that between T_{C2} and H as given in Fig. 3, which disfavors the conclusion that AFI is equivalent to AFII. Similar results have been obtained in Gd_5Ge_4.[23–27] However, for a ZFC process, FM state mixed with AF one is triggered as $\mu_0 H \geq 1.0$ T and a fully FM state is achieved at about 1.6 T in Gd_5Ge_4, which is attributed to the martensitic transformation for the low-temperature AF-to-FM transition. In the title compound, no obvious mixed

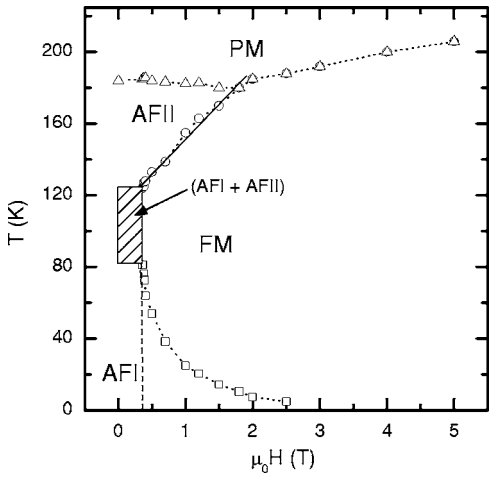

FIG. 3. The magnetic phase diagram for the samples with δ =0.02.

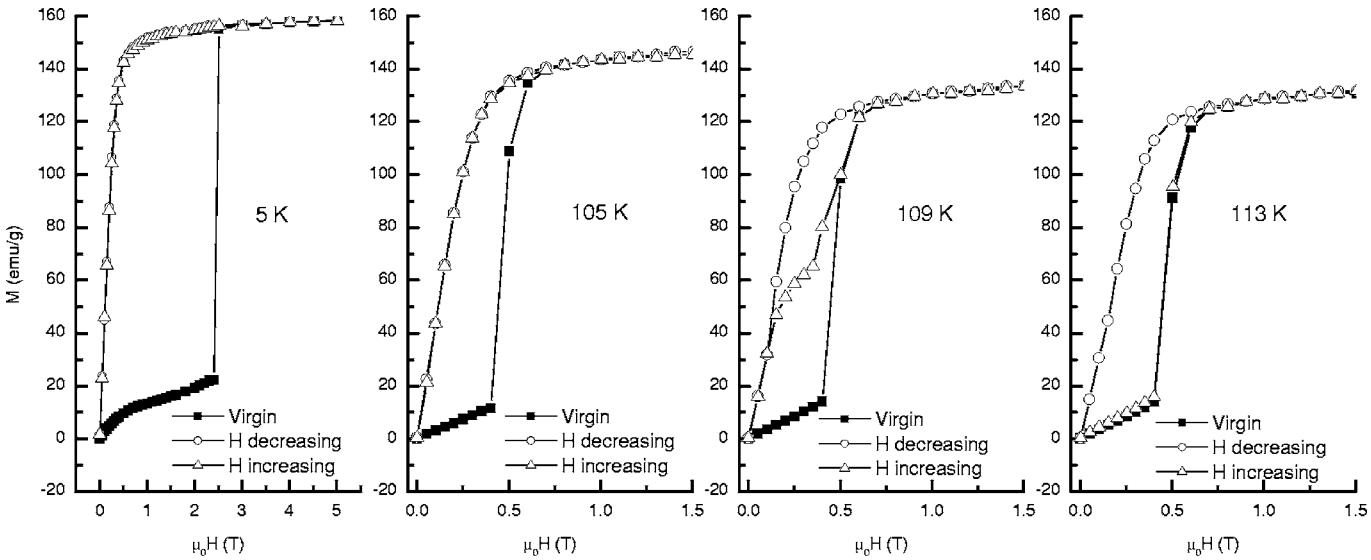

FIG. 4. The magnetization curves at some typical temperatures for the samples with $\delta=0.02$.

state is observed as shown in Fig. 2, which may be due to a standard IEMT.

In order to determine the characteristics of both AFI and AFII, the field-induced transitions are investigated using the magnetization curves. Figure 4 shows the magnetization curves at some typical temperatures. At the temperature below 105 K, the ascending-field magnetization curve superposes the descending-field one, indicative of FM state preserved at zero field after the first magnetizing to FM state. Similar results, which confirm the irreversibility of AF-to-FM transition, have also been found in Gd_5Ge_4 compound.[24,26] Furthermore, it is found that the AFI state can be fully restored only after warming the sample up to 110 K. Thus, the field-induced AFI-to-FM transition is irreversible at $T<105$ K. An AF and FM mixed state is found from the ascending-field magnetization curves at 105 K$<T<$113 K. In the temperature range from 113 to 150 K, the ascending-field magnetizing curves superpose the virgin one. In other words, the hysteresis loop is fully reversible in this temperature range. At the temperature above 150 K, the hysteresis loop disappears.

The heat capacity C_P as a function of temperature was measured at $\mu_0 H=0$ and 0.70 T. For convenience, Fig. 5 shows the curve of C_P/T versus T. The cusp at 183 K is indicative of AFII-to-PM transition, which coincides well with the Néel temperature as shown in Fig. 3. A peak at 138 K, corresponding to T_{C2}, is observed for $\mu_0 H=0.70$ T. However, no peak is found at 39 K, corresponding to T_{C1} under the same field. Because δ is very small, the cluster composed of FeI and 12 FeII is supposed to be ferromagnetic, which is similar to the results in Ref. 4. Thus, the magnetic entropy of AFI (S_M^{AFI}), AFII (S_M^{AFII}) or FM (S_M^{FM}) is much smaller than that of its PM (S_M^{PM}), and the absolute value of ($S_M^{FM}-S_M^{AFI}$) or ($S_M^{FM}-S_M^{AFII}$) is also far smaller than that of ($S_M^{AFII}-S_M^{PM}$). Additionally, for $LaFe_{11.31}Al_{1.69}$ compounds, the results from XRD with and without magnetic field show that the lattice constant in FM state is larger than that in high-temperature AF state and its volume expansion is about 1.0%.[22] Therefore, it is reasonable to deduce that a large volume expansion is followed in the FM-to-AFII transition in this work. As a result, the peak at 138 K as shown in Fig. 5 is mainly contributed by the large change of cell volume, i.e., a large structural entropy change ΔS_L. Consequently, no peak at 39 K is indicative of a neglectable ΔS_L, i.e., a very small change of cell volume. Now, the followed question is what happens in the variation of C_p with temperature at zero field. In a wide temperature range (80–120 K), there is a visible difference between C_p at zero field and that at 0.70 T, which is similar to the results in Gd_5Ge_4 compound.[26] Considering the broadened cusp in the same temperature range as shown in Fig. 1, a probable origin of C_p anomaly shown here is the coexistence of AFI with AFII in the wide temperature range.

In summary, although $LaFe_{11.4}Al_{1.6}$ compound has an AF ground state, $LaFe_{11.4}Al_{1.6}C_\delta$ compounds show a FM ground state at low temperature with $\delta \geq 0.04$. The FM-to-AF tran-

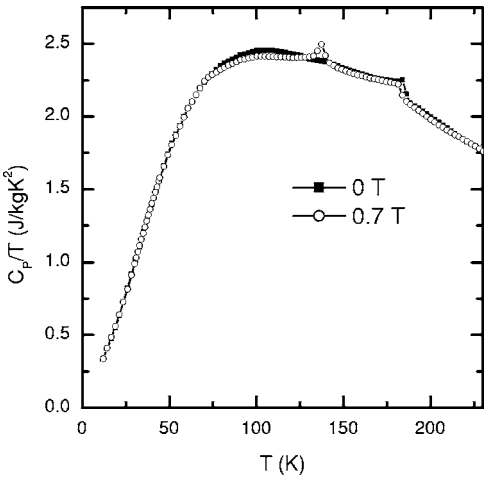

FIG. 5. The heat capacity C_P as a function of temperature at $\mu_0 H=0$ and 0.70 T for the samples with $\delta=0.02$, here C_p/T is used as the ordinate.

sition temperature increases up to the Néel temperature as δ climbs up to 0.08. But, for $\delta=0.02$, there is an AFI-to-AFII transition in a wide temperature range around 100 K at zero field. Although the details of magnetic structures of both AFI and AFII are unknown, the cell volume of AFI is deduced to be larger than that of AFII. At 0.36 T, FM state is induced at the temperature range of AFI-to-AFII transition. T_{C1} decreases and T_{C2} increases with the increase of the field. The AFI-to-FM and AFII-to-FM transitions induced by magnetic field are irreversible and reversible, respectively.

ACKNOWLEDGMENTS

The work was supported by the State Key Project of Fundamental Research and the National Natural Science Foundation of China.

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