Magnetic properties and magnetocaloric effect around phase boundary in $La(Fe_xAl_{1-x})_{13}$ compounds

F. X. Hu[a)]
State Key Laboratory of Magnetism, Institute of Physics and Center of Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100080, People' Republic of China; and Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong

B. G. Shen, J. R. Sun, and G. J. Wang
State Key Laboratory of Magnetism, Institute of Physics and Center of Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100080, People' Republic of China

J. Gao
Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong

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Magnetic properties and magnetocaloric effect (MCE) around phase boundary were investigated in $La(Fe_xAl_{1-x})_{13}$ compounds. We tuned the Fe content from 0.86 to 0.89 and observed a gradual change from ferromagnetic (F) to weak antiferromagnetic (AF) state. A completely F ground state at $x=0.86$ is followed by the emergence of AF coupling at $x=0.87$ and 0.88, in which two spaced transitions appear, one at T_O from F to AF and the other at T_N from AF to paramagnetic state. Continuously increasing Fe to $x=0.89$ results in a completely AF ground state. The magnetic properties of sample $x=0.89$ is especially interesting under an increasing external field. The state under a field of around 3.2 T shows two successive transitions, predicting that two peaks may appear in the temperature dependent magnetic entropy change ΔS. Maxwell relation was employed to calculate ΔS. With the emergence and enhancement of AF coupling, the ΔS profile evolves from a single-peak shape at $x=0.86$ to a nearly constant-peak shape at $x=0.87$ and 0.88, and then to two-peak shape at $x=0.89$. The influence of Fe content on magnetic properties, metamagnetic transition behavior, and MCE is discussed. © *2007 American Institute of Physics*.
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Fe-based cubic $NaZn_{13}$-type (space group $Fm3c$) pseudobinary compounds with the formula $La(Fe_xM_{1-x})_{13}$ ($M=Al, Si$) have attracted much attention[1–6] since the discovery of large magnetocaloric effect (MCE) in this kind of materials.[1,2] The behaviors of itinerant-electron metamagnetic (IEM) transition, magnetic properties, and magnetic entropy change have been systematically investigated in $La(Fe_xSi_{1-x})_{13}$ compounds. It has been demonstrated that field-induced IEM transition above Curie temperature T_C and large lattice expansion during phase transition are responsible for the great MCE observed in $La(Fe_xSi_{1-x})_{13}$ compounds. However, MCE behavior was less reported in $La(Fe_xAl_{1-x})_{13}$ compounds, which possess complex magnetic properties compared to $La(Fe_xSi_{1-x})_{13}$.

$La(Fe_xAl_{1-x})_{13}$ compounds exhibit a unique magnetic phase diagram and different types of magnetic order appear with altering Fe concentration. Micromagnetic states (with ferromagnetic clusters randomly freezed) were found for a low Fe concentration from $x=0.46$ to 0.62, originating from a competition between Fe–Al–Fe antiferromagnetic superexchange coupling and Fe–Fe ferromagnetic direct-exchange coupling. For the Fe concentration ranging from $x=0.62$ to 0.86, the system behaves soft ferromagnetic properties. At Fe concentration from 0.86 to 0.92, an antiferromagnetic character was observed, arising from the similar cause to that in γ-Fe (fcc). A more attractive feature is that such antiferromagnetic state displays a sharp metamagnetic transition, accompanying a significant magnetovolume effect,[7] upon applying a magnetic field of a few teslas. Such a metamagnetic transition will cause a remarkable change in the isothermal magnetic entropy change. Around the ferromagnetic-antiferromagnetic (F-AF) phase boundary in $La(Fe_xAl_{1-x})_{13}$ compounds, large Fe content leads to a high magnetization, and the weak antiferromagnetic coupling leads to a metamagnetic behavior under a low field. These behaviors predict interesting magnetic properties and magnetocaloric effect. In this work, we report the magnetic properties and magnetocaloric effect around the F-AF phase boundary in $La(Fe_xAl_{1-x})_{13}$ compounds. Fe content was tuned from 0.86 to 0.89 and a gradual change from the F state to the weak AF state was observed. It was found that a completely F ground state at $x=0.86$ is followed by the emergence of AF coupling at $x=0.87$ and 0.88, in which two spaced transitions appear. Continuously increasing Fe to $x=0.89$ results in a completely AF ground state. However, the AF coupling at $x=0.89$ is weak and can be easily overcome by applying a low field. It was found that the state under fields near 3.2 T also shows two successive transitions, resulting in an appearance of two peaks in the temperature dependent magnetic entropy change.

a)Electronic mail: hufx@g203.iphy.ac.cn

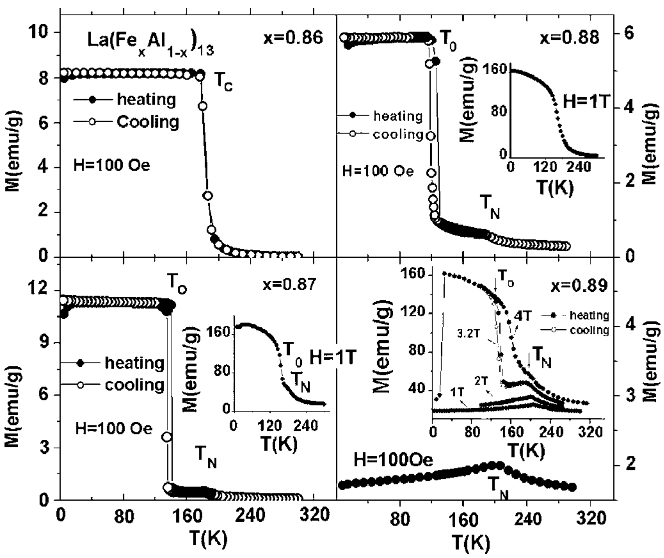

FIG. 1. Temperature dependent magnetization M-T measured under 100 Oe for La(Fe$_x$Al$_{1-x}$)$_{13}$ (x=0.86, 0.87, 0.88, and 0.89) compounds. Insets are M-T curves under relatively high fields for the corresponding samples.

La(Fe$_x$Al$_{1-x}$)$_{13}$ samples were prepared by arc melting technique.[1,2] All magnetic measurements were performed using a superconducting quantum interference device (SQUID) magnetometer.

Temperature dependent magnetization under a low field has been measured in zero-field-cooled (ZFC) and field-cooled (FC) processes in order to determine the magnetic state, the transition temperature, and the nature of the transitions. Figure 1 presents the ZFC-FC magnetization of all samples obtained under a magnetic field of 0.01 T. We found that sample x=0.86 shows completely ferromagnetic ground state with Curie temperature T_C at 183 K. With increasing Fe content, antiferromagnetic coupling appears. Both samples, x=0.87 and x=0.88, exhibit two successive transitions in their ground states. The higher temperature transition with complete temperature reversibility occurs between antiferromagnetism and paramagnetism, while the lower one with a temperature hysteresis happens between ferromagnetism and antiferromagnetism, accompanying a large negative lattice expansion.[7,8] The first-order and second-order nature for the transitions at T_O and T_N, respectively, were manifested from the behavior of ZFC-FC magnetization. The temperature hystereses at T_O were found to be 5 and 10 K for x=0.87 and 0.88 samples, respectively. The AF coupling gradually strengthens as the Fe content increases, leading to an enhancement of the first-order nature and an increase of the magnetic hysteresis at T_O. Previous research indicated that a large amount of Fe atoms will have a fcc-like local environment with 12 nearest neighbors, strongly favoring AF coupling.[9,10] When the Fe content is tuned to x=0.89, a complete AF ground state appears. Néel temperatures T_N obtained from the ZFC-FC mesurements are at 181, 186, and 204 K for x=0.87, 0.88, and 0.89 samples, respectively, indicating the remarkable increase of AF coupling with Fe concentration. However, the AF coupling in the samples is not strong and can be easily overcome by applying a low magnetic field, exhibiting metamagnetic behavior. Insets of Fig. 1 present the temperatrure dependent magnetization measured under relatively high fields for the corresponding samples. The smooth M-T curve, for sample x=0.87, indicates that AF coupling has been fully overcome by 1 T field. However, for sample x=0.88, an inflexion at T_N is still visible, indicating that AF coupling remains under 1 T. For the case of x =0.89, AF coupling becomes so strong that a field lower than 2 T cannot cause any spin flips. With increasing field from 0.01 to 3.2 T, T_N decreases from 204 to 189 K, indicating that the AF coupling becomes weak with applied field. For the case that a field of 3.2 T is applied, metamagnetic transition from AF to F state takes place and two successive transitions appear, similar to the ground states in samples x=0.87 and 0.88, predicting that two-peak-like magnetic entropy change may occur. A shoulder at T_N is still visible even the field is increased to 4 T, indicating that AF coupling still remains under 4 T.

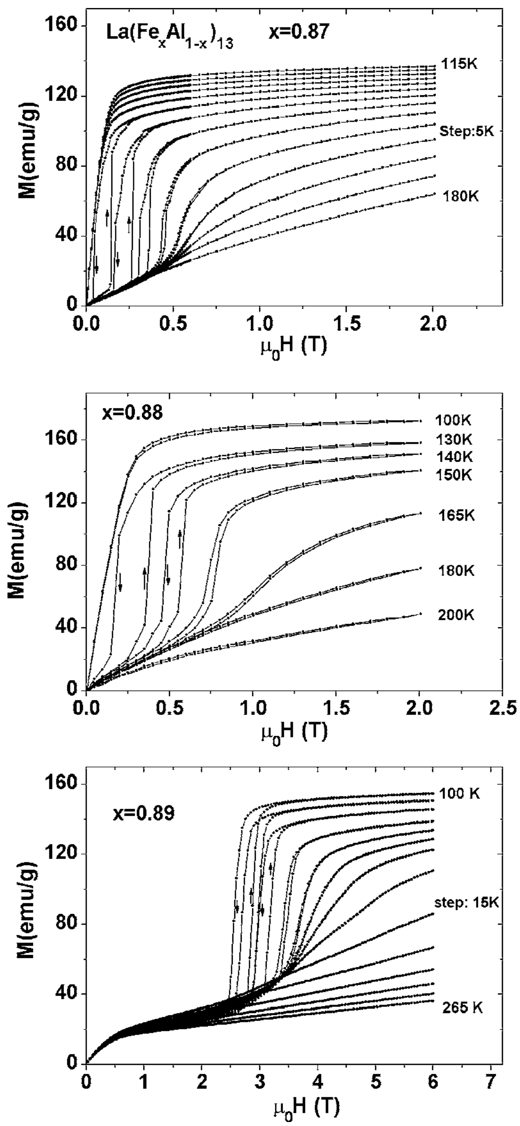

FIG. 2. Magnetization isotherms M-H for La(Fe$_x$Al$_{1-x}$)$_{13}$ (x=0.87, 0.88, and 0.89) compounds measured upon magnetic field increase and decrease.

Figure 2 presents the magnetization isotherms M-H for samples x=0.87, 0.88, and 0.89. (M-H isotherms of x=0.86 are not shown here, it shows a typical soft ferromagnetic

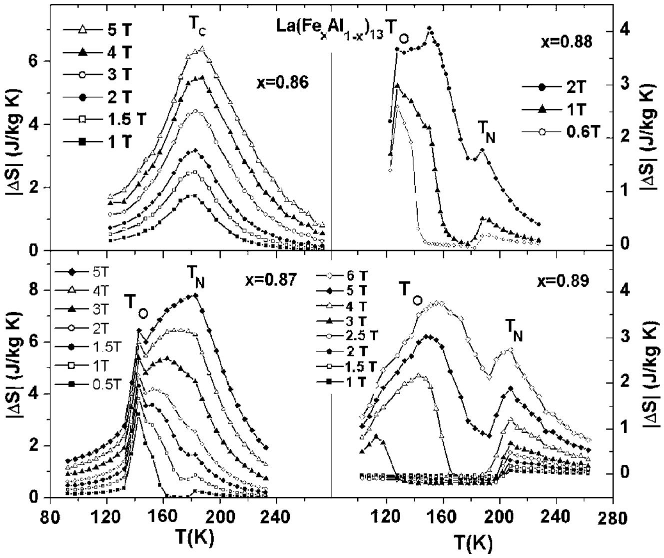

FIG. 3. Magnetic entropy change ΔS as functions of temperature and magnetic field for $La(Fe_xAl_{1-x})_{13}$ (x=0.86, 0.87, 0.88, and 0.89) compounds.

behavior). To clearly exibit the metamagnetic behavior, the isotherms on a cycling of field increase and decrease are given. Above a critical field H_C, a sharp change of magnetization with a hysteresis occurs for the three samples, which means that a field-induced metamagnetic transition from an AF to a F state takes place. With increasing temperature the hysteresis width becomes narrower and the critical transition field H_C increases. For similar temperatures, the increased critical field in the samples with a higher Fe concentration verifies a much stronger AF coupling. For sample x=0.89, a magnetic field lower than 2 T cannot induce any metamagnetic transitions for all temperatures, which is consistent with the M-T measurements taken under relatively high fields [inset of Fig. 1(d)].

According to thermodynamical theory, magnetic entropy change $\Delta S(T,H)$ is given by the Maxwell relation[11–13] $\Delta S(T,H)=S(T,H)-S(T,0)=\int_0^H (\partial M/\partial T)_H dH$. Figure 3 shows the magnetic entropy change ΔS as a function of temperature and magnetic field. It is found that with the emergence and enhancement of AF coupling, ΔS profile evolves from a single peak at x=0.86 to a nearly constant peak at x=0.87 and 0.88, and then to a two-peak-like at x=0.89. The second-order nature of the magnetic transition in sample x=0.86 prescripts a λ-like shape of ΔS peaking at T_C $\sim$183 K. With the emergence and enhancement of AF coupling in x=0.87 and 0.88 samples, two close transitions appear. Field-induced metamagnetic transition from AF to F state above T_O leads to an asymmetric broadening of ΔS to higher temperature, which is overlapped with the contribution from the transition at T_N, resulting in a nearly constant peak in ΔS. The ΔS magnitude for samples x=0.86 and 0.87 is considerably large compared with the previous materials in the similar temperature range,[13] originating from the high magnetization and a low critical field for inducing the metamagnetic transitions. With increasing Fe content AF coupling becomes stronger and stronger, and the critical field for inducing the metamagnetic transition becomes higher and higher. For the case of x=0.89, a field lower than 2.5 T cannot cause any metamagnetic transitions, thus no contributions to ΔS were found around T_O for a field below 2.5 T. As the external field is increased to 3 T, metamagnetic transition from AF to F state takes place and a small ΔS peak grows around T_O. Because of the relatively large space between the two transitions at T_O and T_N, ΔS shapes two-peak-like even when the field is increased to 6 T. With increasing field no saturation trend of ΔS was found. It can be expected that ΔS of sample x=0.89 would become also nearly constant in the region between T_O and T_N when the external field is increased to a considerable value. One knows that an appropriate ΔS profile with a constant (or almost constant) value through the thermodynamical cycle range is specially desired for Ericsson-cycle refrigerator.

In conclusion, the development of magnetic properties and magnetocaloric effect with tuning Fe concentration is systematically investigated in $La(Fe_xAl_{1-x})_{13}$ compounds. At the high coordination numbers of Fe atoms, F order will become unstable and the AF state is strongly favored. With the emergence and enhancement of AF coupling, ΔS profile evolves from a single peak at x=0.86 to a nearly constant ΔS at x=0.87 and 0.88, and then to two-peak-like ΔS at x=0.89. Sample x=0.86 shows completely ferromagnetic ground state with T_C at 183 K. With increasing Fe content antiferromagnetic coupling appears. Both samples of x=0.87 and 0.88 exhibit two closed transitions in their ground state, leading to a nearly constant magnetic entropy change, which is specially desired for the Ericsson-cycle refrigerator. When the Fe content is tuned to x=0.89, a complete AF ground state appears. However, the AF coupling is not strong and can be easily overcome by applying a magnetic field of a few teslas, exhibiting metamagnetic behavior. The state under fields near 3.2 T also shows two successive transitions for sample x=0.89, leading to the two-peak-like ΔS.

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