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Magnetic properties and magnetocaloric effect in $Nd_xLa_{1-x}Fe_{11.5}Al_{1.5}$ compounds*

Wang Fang(王 芳)†, Wang Guang-Jun(王光军),
Sun Ji-Rong(孙继荣), and Shen Bao-Gen(沈保根)

State Key Laboratory of Magnetism, Institute of Physics and Centre for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100190, *China*

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Effects of Nd-doping on the magnetic properties and magnetocaloric effects (MCEs) of $Nd_xLa_{1-x}Fe_{11.5}Al_{1.5}$ have been investigated. Substitution of Nd leads to a weakening of the antiferromagnetic (AFM) coupling and an enhancement of the ferromagnetic (FM) coupling. This in turn results in a complex magnetic behaviour for $Nd_{0.2}La_{0.8}Fe_{11.5}Al_{1.5}$ characterized by the occurrence of two phase transitions at ∼188 K (PM–AFM) and ∼159 K (AFM–FM). As a result, a table-like MCE (9 J/kg·K) is found in a wide temperature range (160–185 K) for a field change of 0–5 T around the transition temperature, as evidenced by both the magnetic and calorimetric measurements. Based on the analysis of low-temperature heat capacity, it is found that the AFM–FM phase transition modifies the electron density significantly, and the major contribution to the entropy change comes from the electronic entropy change.

Keywords: magnetic properties, $NaZn_{13}$-type compounds, magnetic entropy change
PACC: 7530S, 6540, 7550E, 0570F

$NaZn_{13}$-type LaFe-based compounds $La(Fe,Si)_{13}$ and $La(Fe,Al)_{13}$ have recently attracted much attention due to their potential applications in magnetic refrigeration.[1−3] $La(Fe,Al)_{13}$ compounds with different Al content show diverse magnetic properties, and their properties are easily modified by magnetic field, pressure, temperature and composition.[4−11] The ground magnetic state of $La(Fe,Al)_{13}$ compounds with high Fe concentration is antiferromagnetic. Substitution of small amounts of Co for Fe or introducing carbon atoms can make the antiferromagnetic coupling collapse and result in a ferromagnetic state.[12−19] Large magnetic entropy change is observed around the phase transition temperature without any hysteresis, which indicates that they may be an appropriate candidate for the magnetic refrigerant. To date, limited reports are available about the effects of other rare earth elements in $La(Fe,Al)_{13}$ compounds with high Fe concentration on the structure, phase transition and magnetic properties.

In this paper, we use light rare earth element Nd to substitute for La and investigate the change of magnetic properties in detail. In addition, a table-like magnetocaloric effect (MCE) (9 J/kg·K) is found in a wide temperature range (160–185 K) for a field change of 0–5 T around the transition temperature, as evidenced by both the magnetic and calorimetric measurements. We also carry out a study on the origin of this large entropy change by combined magnetic and calorimetric measurements.

Arc-melted samples $Nd_xLa_{1-x}Fe_{11.5}Al_{1.5}$ (x=0–0.5) were annealed at 1173K for 2 weeks in vacuum, then quenched in liquid nitrogen. X-ray diffraction was used to examine the phase purity of the compounds. The dc magnetization, ac susceptibility at different frequencies and heat capacity were measured using a physical property measurement system (PPMS) in the temperature range 2–295 K under applied fields up to 8 T.

X-ray diffraction patterns of compounds $Nd_xLa_{1-x}Fe_{11.5}Al_{1.5}$ (x=0, 0.1, 0.2 and 0.3) at room temperature are shown in Fig.1. One can see that the compounds $Nd_xLa_{1-x}Fe_{11.5}Al_{1.5}$ (x=0.1 and 0.2) obtained are single-phase with a cubic $NaZn_{13}$-type structure. When $x \geq 0.3$, the alloys are mixtures containing mainly $Nd_{1-x}La_xFe_{11.5}Al_{1.5}$ and α-Fe, which

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†E-mail: wangfang@g203.iphy.ac.cn

suggests that the substitution of Nd for La makes the compounds less stable. The lattice parameter a decreases slightly with increasing x due to the lanthanide contraction, and their values are 1.15917 nm, 1.15857 nm and 1.15836 nm for x=0, 0.1 and 0.2, respectively. It indicates that we have successfully introduced Nd atoms into the La–Fe phase.

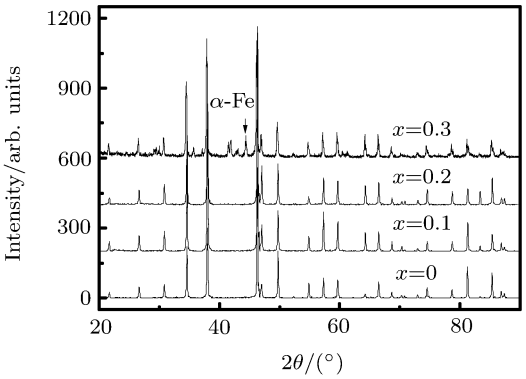


Fig.1. X-ray diffraction patterns of compounds $Nd_xLa_{1-x}Fe_{11.5}Al_{1.5}$ (x=0, 0.1, 0.2 and 0.3) at room temperature.

Temperature dependence of magnetization ($M-T$) for $Nd_xLa_{1-x}Fe_{11.5}Al_{1.5}$ compounds has been measured under a field of 0.01T, and both the $M-T$ curves of zero-field-cooled (ZFC) and field-cooled (FC) modes are shown in Fig.2. It is found that $LaFe_{11.5}Al_{1.5}$ compound is antiferromagnetic (AFM) with the Néel temperature T_N=205 K. And a broad cusp is observed around 85K in the ZFC curve with x=0.1 and a distinct separation between FC and ZFC curves appears below T_N. Both $M-T$ (under different applied magnetic fields up to 5 T), as shown in Fig.3(a) and $M-H$ (at different temperature 5–220 K), as shown in Fig.3(b) curves reveal that the competition between AFM and FM orders is very strong, which usually results in a spin-glass or cluster glass behaviour. One finds that the remanent magnetization is time-dependent, which is also characteristic of spin glass.[20] To verify the magnetic state below 85 K, we have measured the ac susceptibility at different frequencies ranging from 500 to 10000 Hz (not shown here). No frequency dependence of the cusp position is found in the temperature dependence of the real component of the ac susceptibility ($\chi-T$) curve, which excludes the presence of spin glass state.[21] Combining the ac and dc measurement results, we can conclude that some large FM clusters are formed in the AFM background and its magnetic state is very sensitive to the applied field and temperature. The FM coupling enhances and the AFM coupling weakens under the applied field. When H=0.5 T, it is AFM below 42 K, FM in the temperature range between 42 and 121 K, and AFM reappears again at higher temperatures up to 199 K and it is PM above 199 K. When H=2 T, it

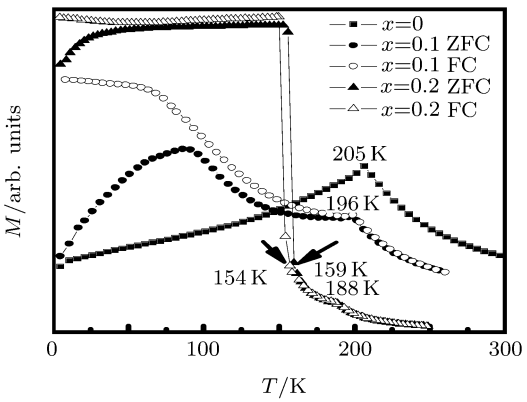
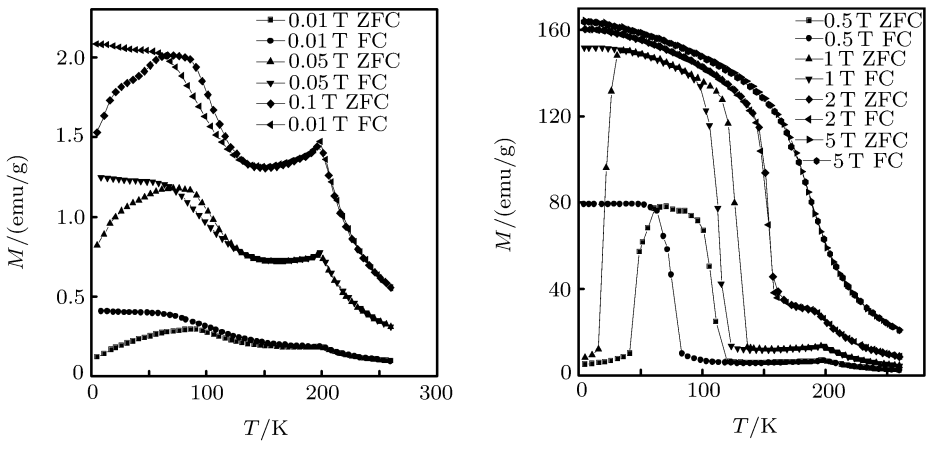
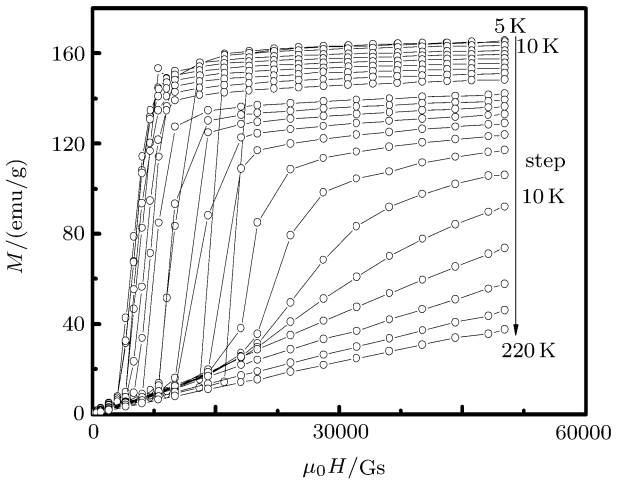


Fig.2. Temperature dependence of zero-field-cooled (ZFC) and field-cooled (FC) magnetization $M-T$ curve at 0.01 T for $Nd_xLa_{1-x}Fe_{11.5}Al_{1.5}$ (x=0, 0.1 and 0.2) compounds.



(a)



(b)

Fig.3. (a) Temperature dependence of magnetization $M-T$ for $Nd_{0.1}La_{0.9}Fe_{11.5}Al_{1.5}$ under different applied magnetic fields up to 5 T, (b) Field dependence of magnetization $M-H$ for $Nd_{0.1}La_{0.9}Fe_{11.5}Al_{1.5}$ (at different temperature between 5–220 K).

is completely FM below 140 K and FM–AFM transition and AFM–PM transition occurs at 155K and 190 K, respectively. When H=5 T, the two transitions merge into one, no clear AFM is observed. A schematic magnetic phase diagram ($T-H$) is constructed as shown in Fig.4.

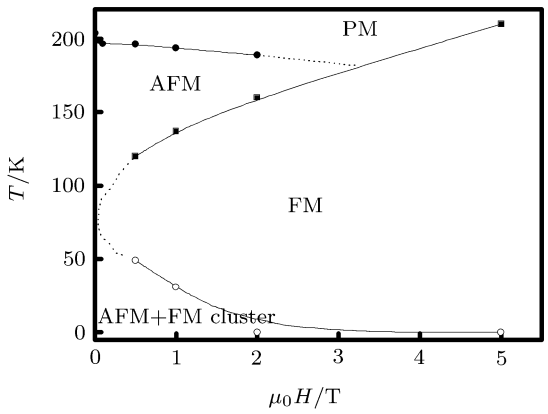


Fig.4. A schematic magnetic phase diagram ($T-H$) of compound $Nd_{0.1}La_{0.9}Fe_{11.5}Al_{1.5}$.

For the compound $Nd_{0.2}La_{0.8}Fe_{11.5}Al_{1.5}$, a second-order PM–AFM transition, which is thermally reversible, and a first-order AFM–FM transition with substantial thermal hysteresis occurs at 188 and 159 K, respectively. And a separation appears below 50 K between the FC and ZFC curves.

Figure 5 shows the isothermal $M-H$ curves of $Nd_xLa_{1-x}Fe_{11.5}Al_{1.5}$ compounds at 5K. In the field increasing mode, for compound $LaFe_{11.5}Al_{1.5}$, a sharp metamagnetic AFM-FM transition occurs at the critical field 5.8 T. A strong magnetic hysteresis is found, which can be attributed to the overcooling of FM state during the field decreasing. The critical field decreases from 5.8 T to 1.9 T with x increasing from 0 to 0.1, and a typical FM behaviour is found at x=0.2.

From the above results we can propose that some large FM clusters are formed in the AFM background for compound $Nd_{0.1}La_{0.9}Fe_{11.5}Al_{1.5}$, and it is almost FM for $Nd_{0.2}La_{0.8}Fe1_{1.5}Al_{1.5}$, which shows that the substitution Nd for La can weaken the AFM coupling and enhance the FM coupling. We explain it as follows.

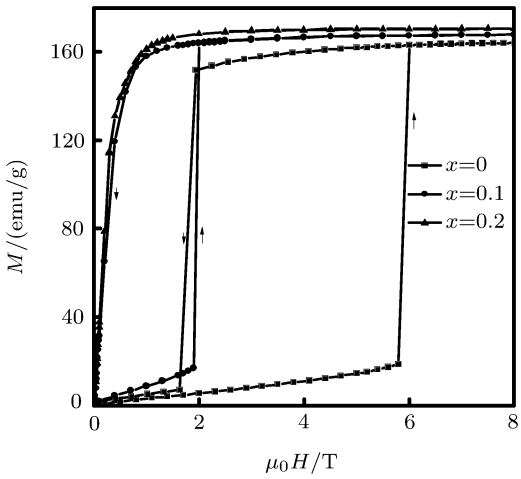


Fig.5. Isothermal $M-H$ curves of $Nd_xLa_{1-x}Fe_{11.5}Al_{1.5}$ compounds at 5 K with field increase and decrease modes.

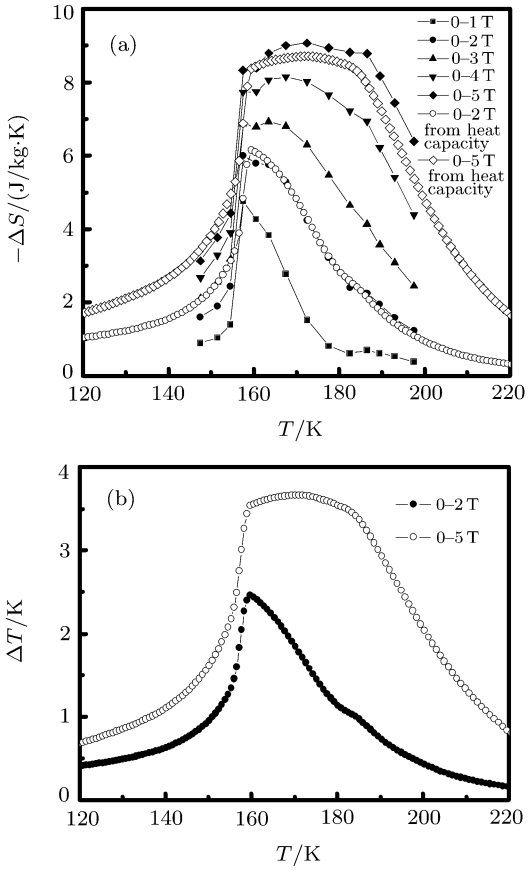


Fig.6. (a) Temperature dependence of entropy change at various field changes calculated from both magnetic and calorimetric methods for $Nd_{0.2}La_{0.8}Fe_{11.5}Al_{1.5}$, (b) Temperature dependence of the adiabatic temperature change ($\Delta T_{ad} - T$) for field changes of 0–2 T and 0–5 T for $Nd_{0.2}La_{0.8}Fe_{11.5}Al_{1.5}$.

In $LaFe_{11.5}Al_{1.5}$ compound, the average iron-iron exchange interaction is negative and strongly dependent of the Fe–Fe bond length. After introducing the magnetic rare earth elements Nd, their magnetic properties depend not only on the Fe–Fe distance but also on the effects of Nd. As is known, in rare earth-transition metal (RE-T) compounds, the coupling between the heavy rare earth element and transition metal should be negative, and it is positive for light rare earth element such as Ce, Pr and Nd. The positive 3d–4f exchange interaction between RE and Fe will weaken the AFM coupling. When the RE concentration is small, the AFM coupling cannot be destroyed completely, only some FM clusters are formed in the AFM background, such as in $Nd_{0.1}La_{0.9}Fe_{11.5}Al_{1.5}$. With increasing Nd concentration, the Nd–Fe FM coupling pairs increase and the AFM coupling collapses finally. Furthermore, the smaller radius of Nd atom causes the lattice distortion, and thus affects the Fe–Fe, Fe–Al–Fe bond lengths and the Fe–Al–Fe bond angle, which finally weakens the AFM coupling.

Previous reports have shown that $La(Fe,Al)_{13}$ compounds (such as $LaFe_{11.44}Al_{1.56}$) with two adjacent phase transitions can exhibit large magnetic entropy change in a very wide temperature range,[22] which is very useful in the Ericsson cycle. For compound $Nd_{0.2}La_{0.8}Fe_{11.5}Al_{1.5}$, the PM–AFM and AFM–FM transitions occur at 188 and 159 K, respectively. It is possible that $Nd_{0.2}La_{0.8}Fe_{11.5}Al_{1.5}$ would show similar behaviour. So, we have studied their entropy change ΔS and the adiabatic temperature change ΔT_{ad} properties using both magnetic and calorimetric methods.

The isothermal $M - H$ curves were measured around the critical temperatures. The magnetic entropy change $|\Delta S|$ is calculated from the Maxwell relation $\Delta S(T,H) = -\int (\partial M/\partial T)_H \mathrm{d}H$ using the collected magnetization data.[23] The specific heat was measured over the temperature range 2–295 K under the applied field of 0, 2 and 5 T. $|\Delta S|$ and $|\Delta T_{ad}|$ can be calculated based on the following equations[18]

$$S(T) = \int_0^T \frac{C(T)_H}{T}\mathrm{d}T + S_{0,H},$$

$$\Delta S = S(H,T) - S(0,T),$$

$$S(T + \Delta T, B = \Delta B + B1) = S(T, B1).$$

Figure 6(a) displays the temperature dependence of $|\Delta S|$ for various field changes calculated by both methods. The two techniques yield consistent results. When the applied field changes are smaller than 3 T, two peaks were found in the $\Delta S - T$ curves. The one at the lower temperature originates from the first-order transition FM–AFM, which increases and broadens to the higher temperature with increasing applied field change. The one at the higher temperature originates from the second-order transition, which increases quickly and moves to the low temperatures with increasing applied field change. The two peaks merge into a broad one at the field change of 0–5 T. A table-like MCE is found in a wide temperature range (160–185 K) for a field change of 0–5 T around the transition temperature. It is comparable to that of gadolinium.[24] The full width at half maximum $\mathrm{d}T_{FWHM}$ is almost 50 K and the relative cooling power (RCP) is about 376 J/kg. Temperature dependence of the adiabatic temperature change ΔT_{ad} obtained from calorimetric method is shown in Fig.6(b).

It is 3.7 K at 0–5 T around the phase transition temperature.

The FM–AFM first-order transition is from one fully ordered state to another fully ordered state. Since the magnetic entropy is a measurement of the magnetic order, there should not be large difference of magnetic entropy between FM and AFM state. Obvious large entropy change, however, is obtained by both magnetic and calorimetric methods. It is necessary to give a further analysis of the origin of this large entropy change. As is known, the total entropy of magnetic materials is composed of three parts: the magnetic entropy S_M, the lattice entropy S_L and the electron entropy S_e. In general, all three contributions depend on temperature and magnetic field and cannot be clearly separated. A similar phenomenon was also observed in FeRh alloy. Annaorazov *et al*[25] pointed out that the change in the electronic part of the entropy makes a dominative contribution to the AFM–FM transition in the FeRh alloy.

It is a little hard to obtain the accurate electronic information around the phase transition range, since the electronic specific heat C_e is much smaller than the lattice specific heat C_L. $LaFe_{11.5}Al_{1.5}$ and $Nd_{0.2}La_{0.8}Fe_{11.5}Al_{1.5}$ compounds have almost the same composition and their electronic specific heat should be very close in the same magnetic state. To estimate the electronic contribution to the entropy change, we measured the specific heat over the temperature range 2–295 K for both compounds, and $C_p/T - T^2$ is shown in Fig.7. In the low temperature range, $C_e = \gamma T + \beta T^3$ plays a major role, where γ is the Sommerfeld coefficient, $\beta = \dfrac{12\pi^4 R}{5\theta_D^3}$, θ_D is the Debye temperature and R=8.31J/(molK). A best fit of the specific heat data below 20 K using $C_e = \gamma T + \beta T^3$ was obtained in both compounds. γ_{AFM} for $LaFe_{11.5}Al_{1.5}$ and γ_{FM} for $Nd_{0.2}La_{0.8}Fe_{11.5}Al_{1.5}$ is 0.23557 and 0.27038 J/kg·K^2, respectively. This implies that the phase transition modifies the electron density significantly. Then the contribution of Se is obtained from the relation $\Delta S_e = (\gamma_{AFM} - \gamma_{FM}) \times T_F$. It is –5.6 J/kg·K, which is comparable to the total entropy change. We can see that, the main entropy change around the FM–AFM phase transition comes from the electronic entropy change.

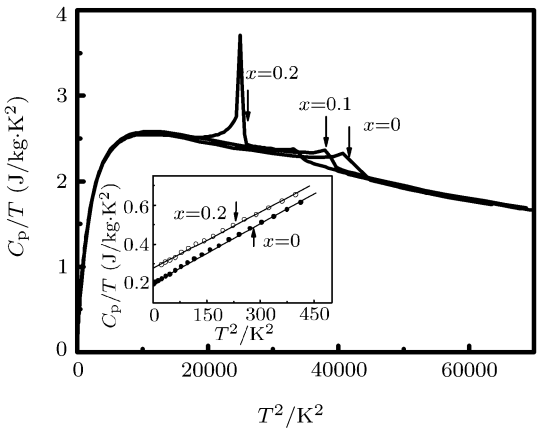


Fig.7. $C_p/T - T^2$ for compounds $Nd_xLa_{1-x}Fe_{11.5}Al_{1.5}$ (x=0, 0.1 and 0.2). The inset shows the simulated results using $C_e = \gamma T + \beta T^3$ in low temperature range.

In conclusion, the effects of light rare earth elements substitution for La in compound $LaFe_{11.5}Al_{1.5}$ on the magnetic properties have been investigated in detail. The cubic $NaZn_{13}$-type structure pertains only to the small substitution case and the lattice parameter decreases slightly due to the lanthanide contraction. The positive 3d–4f exchange interaction between RE and Fe weakens the AFM coupling. When the RE content is small, the AFM coupling cannot be destroyed completely, only some FM clusters are formed in the AFM background, such as in $Nd_{0.1}La_{0.9}Fe_{11.5}Al_{1.5}$. $Nd_{0.2}La_{0.8}Fe_{11.5}Al_{1.5}$ exhibits two phase transitions at 188K(PM–AFM) and 159K (AFM–FM). A table-like MCE is found in a wide temperature range (160–185 K) for a field change of 0–5 T around the transition temperature, as evidenced by both the magnetic and calorimetric methods. Based on the analysis of heat capacity in low temperature range, we have found that the AFM–FM phase transition modifies the electron density significantly. And the major contribution to this large entropy change comes from the electronic entropy change.

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