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Effects of Fe–Fe bond length change in $NaZn_{13}$-type intermetallic compounds on magnetic properties and magnetic entropy change*

Wang Guang-Jun(王光军)†, Hu Feng-Xia(胡凤霞),
Wang Fang(王 芳), and Shen Bao-Gen(沈保根)

State Key Laboratory of Magnetism, Institute of Physics and Center of Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100080, *China*

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In this paper the effects of Fe–Fe bond length change on magnetic properties and magnetic entropy change have been investigated on $LaFe_{12.4-x}Si_xCo_{0.6}$ and $LaFe_{12.3-x}Al_xCo_{0.7}$ intermetallic compounds. According to the analyses of Fe–Fe bond length change, the variation of Curie temperature and the unusual magnetic phase transition which results in the large magnetic entropy change were explained. The effects of the substitution of Co and Si for Fe on magnetic entropy change and field-induced itinerant-electron metamagnetic transition in $LaFe_{12.4-x}Si_xCo_{0.6}$ compounds were also studied and the considerable magnetic entropy change has been achieved.

Keywords: Fe–Fe bond length, magnetic phase transition, magnetic entropy change
PACC: 7530S, 7550B

1. Introduction

Room-temperature magnetic refrigerants with a large magnetocaloric effect (MCE) have attracted much attention in recent years due to their potential applications in magnetic refrigeration technique.[1] Rare earth metals and compounds having second-order or first-order magnetic transitions have been investigated in an attempt to find materials with a large MCE. Rare earth metal Gd with second-order magnetic phase transition was considered before to be the best room-temperature refrigerant,[2] but recently materials with first-order magnetic transition have been found to display larger magnetic entropy, such as $Gd_5Si_2Ge_2$,[2] $MnAs_{1-x}Sb_x$[3] and $MnFeP_{1-x}As_x$.[1]

The large magnetic entropy change and giant isotropic magnetostriction of the $NaZn_{13}$-type Fe-based compounds have also been studied in detail.[4−11] In $LaFe_{13-x}Si_x$ compounds,[4−5] experimental results show that the large magnetic entropy change in them decreases gradually with increasing x, and the magnetic transition changes gradually from first-order to second-order.

Though some macroscopic theories have been attempted to describe the magnetic entropy change,[12,13] there are not sufficient investigations on the microscopic mechanism of the entropy change. In the present work, we try to give some explanation, based on the studies of Fe–Fe bond lengths, for the magnetic entropy change and the change of transition feature in $NaZn_{13}$-type Fe-based compounds.

Previous investigations[14−19] have shown that the magnetic properties of the R-Fe-based compounds are determined predominantly by the Fe–Fe interaction, which is sensitive to the Fe–Fe distance and the number of nearest neighbours. This is different from the behaviours of R-Co(Ni)-based compounds, which are essentially determined by the modification of Co(Ni) electronic configuration caused by the transfer of rare-earth conduction electrons to the transition metal 3d band.[17,18]

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†Corresponding author: gjwang@g203.iphy.ac.cn

The Fe–Fe bond length change also has effect on the magnetic properties of $NaZn_{13}$-type intermetallic compounds. In this paper, we prepare compounds $LaFe_{12.4-x}Si_xCo_{0.6}$ and $LaFe_{12.3-x}Al_xCo_{0.7}$ and study the effects of Fe–Fe bond length change on the magnetic properties and magnetic entropy change. The substitution of Co for Fe is expected to be able to increase their Curie temperature T_C.

2. Experimental details

$LaFe_{12.4-x}Si_xCo_{0.6}$ (x=1.1–2.3) and $LaFe_{12.3-x}Al_xCo_{0.7}$ (x=1.30–4.68) samples were prepared by arc melting in an atmosphere of ultrapure argon gas. The purity of the four starting elements was better than 99.9wt%. The ingots were remelted three times to ensure homogeneity, annealed in vacuum at 1273K for 50 days and then quenched in liquid nitrogen.

Step-scan powder x-ray diffraction (XRD) with Cu$K\alpha$ radiation was used to determine the lattice parameters, phases present and the Fe–Fe distance. All the magnetic measurements were carried out with an MPMS-7 type superconducting quantum interference device (SQUID) magnetometer. Thermomagnetic measurements at a low field of 0.05T in the zero-field-cooled (ZFC) process provided reliable information about the values of T_C.

In order to calculate the magnetic entropy change ΔS of the samples, the M–H curves in a wide temperature range were measured at different field and temperature steps.

3. Results and discussion

Step-scan powder XRD results were obtained using Rietica computer program based on Rietveld [20,21] refinement of XRD data. The results indicated that $LaFe_{12.3-x}Co_{0.7}Al_x$ and $LaFe_{12.4-x}Si_xCo_{0.6}$ compounds crystallize in the cubic $NaZn_{13}$-type single phase with a space group $Fm\bar{3}c$ (O_h^6) and Z=8. In the hypothetical compound $LaFe_{13}$, the La atoms occupy 8(a) (0.25, 0.25, 0.25) site and the Fe atoms occupy two different sites, 8(b) (0, 0, 0) and 96(i) (0, y, z) for Fe^I and Fe^{II}, respectively. So the Fe–Fe bond lengths are determined completely by the coordinate (0, y, z) and the lattice parameter. There are five different Fe–Fe interatomic distances between the nearest neighbours of Fe atoms. One is $\sqrt{x^2+y^2}a$ for Fe^I–Fe^{II} and the other four distances between Fe^{II} and Fe^{II} are denoted as A ($2za$),

$$B(\sqrt{y^2+z^2+(y-z)^2}a),$$
$$C(\sqrt{(y-z)^2+(0.5-y-z)^2}a)$$

and

$$D(\sqrt{2z^2+(0.5-2y)^2}a).$$

Here a is the lattice parameter and the expressions in the brackets are the Fe–Fe bond lengths. Figure 1 shows the distribution of the five Fe–Fe bonds around the Fe^{II} atom, which occupies the 96(i) site. The relative fractions of these atomic distances are Fe^I–Fe^{II}:A:B:C:D=2:1:4:2:2.

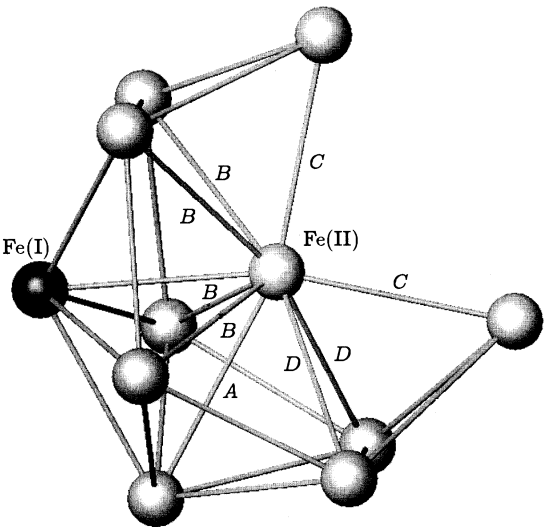


Fig.1. The distribution of the five Fe–Fe bonds around the Fe^{II} atom in the hypothetical compound $LaFe_{13}$.

In Figs.2 and 3 the Si(Al) concentration dependence of the room-temperature lattice parameters and the Fe–Fe bond lengths is shown for $LaFe_{12.4-x}Si_xCo_{0.6}$($LaFe_{12.3-x}Al_xCo_{0.7}$) compounds. Since the atomic radius of Fe atom is larger than that of Si and smaller than that of Al, substitution of Si leads to the contraction of the unit-cell volume, while substitution of Al leads to a dilation.

Though the variations of lattice parameters in the two series compounds are contrary to each other, the Curie temperatures have both increased with the increase of Si(Al) concentration in the region of low Si(Al) concentration. In Fig.4 the Si(Al) concentration dependence of Curie temperature is displayed. In order to understand how the reverse variation of lattice parameters leads to the same variation of Curie temperatures, we have investigated in detail the change of the Fe–Fe bond lengths.

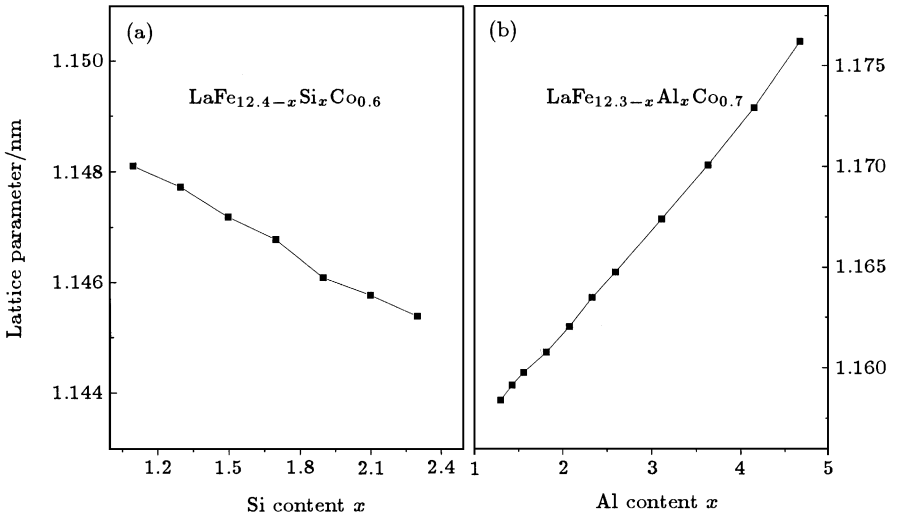


Fig.2. The Si(Al) concentration dependence of the room-temperature lattice parameter for $LaFe_{12.4-x}Si_xCo_{0.6}$($LaFe_{12.3-x}Al_xCo_{0.7}$) compounds.

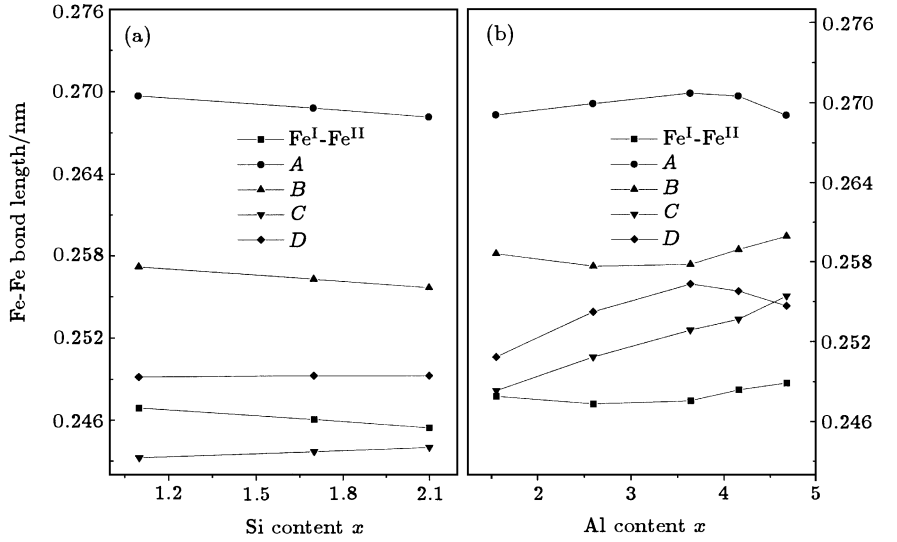


Fig.3. The Fe–Fe bond length versus the Si(Al) concentration in the $LaFe_{12.4-x}Si_xCo_{0.6}$ ($LaFe_{12.3-x}Al_xCo_{0.7}$) compounds.

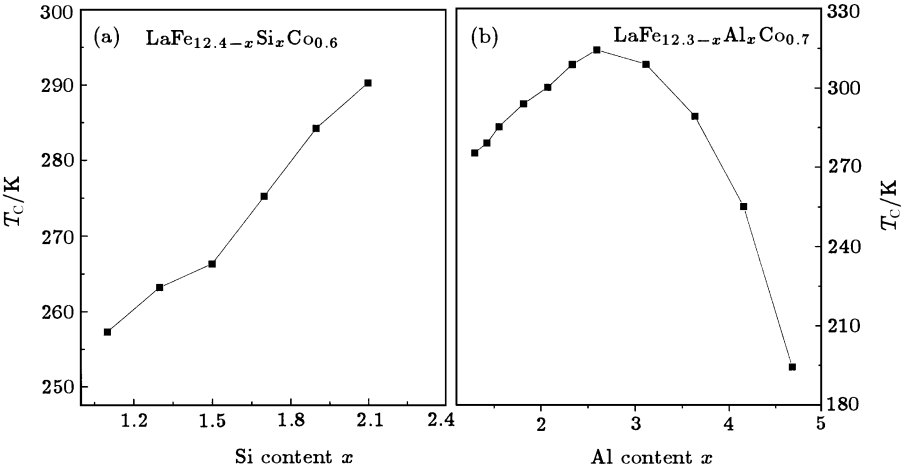


Fig.4. The Curie temperature versus the Si(Al) concentration in the $LaFe_{12.4-x}Si_xCo_{0.6}$ ($LaFe_{12.3-x}Al_xCo_{0.7}$) compounds.

Similar to the results of Néel and Slater,[22] the results of Givord [18] and Wang [19] show that the variation of $J_{\mathrm{Fe-Fe}}$ with Fe–Fe interatomic distance is as follows: $J_{\mathrm{Fe-Fe}}$ is negative when Fe–Fe interatomic distance is below 0.244nm, gradually increases with increasing distance and achieves the maximum value at 0.255nm. Here $J_{\mathrm{Fe-Fe}}$ is the ferromagnetic Fe–Fe exchange interaction parameter.

Since the optimal value of the Fe–Fe bond length to contribute to the Fe–Fe exchange interaction is about 0.255nm,[19] the elongation of the Fe–Fe bond lengths shorter than 0.255nm and the shortening of the Fe–Fe bond lengths longer than 0.255nm both strengthen the exchange interaction and increase $J_{\mathrm{Fe-Fe}}$. On the other hand, the elongation of the bond lengths longer than 0.255nm and the shortening of the bond lengths shorter than 0.255nm both weaken the exchange interaction and decrease $J_{\mathrm{Fe-Fe}}$. The competition between the two opposite effects determines the variation of total $J_{\mathrm{Fe-Fe}}$.

In $LaFe_{12.4-x}Si_xCo_{0.6}$ compounds, all except the Fe^{I}–Fe^{II} bond length become gradually close to 0.255nm. According to the distance dependence of the Fe–Fe exchange interaction, the variations of the four (A, B, C and D) bond lengths enhance the Fe–Fe exchange interaction, but that of the Fe^{I}–Fe^{II} bond length weakens the interaction. The competition of the two effects leads to the increase of total $J_{\mathrm{Fe-Fe}}$ due to the small relative fraction of the Fe^{I}–Fe^{II} bond.

Similarly, in the region of the low Al concentration in $LaFe_{12.3-x}Al_xCo_{0.7}$ compounds, the B, C and D bond lengths change rapidly with increasing Al concentration, and they all enhance the Fe–Fe exchange interaction. Though the change of the Fe^{I}–Fe^{II} and A bond lengths weaken the interaction, this change is small and has little effect on the interaction. So the total $J_{\mathrm{Fe-Fe}}$ also increases with increasing Al concentration in the region of low Al concentrations.

For nonmagnetic light rare-earth La element, one may neglect the R–R and R–T interactions relative to the T–T interaction and then the Curie temperature in the $NaZn_{13}$-type Fe-based compounds is determined by the following three factors: (1) the Fe–Fe ferromagnetic exchange interaction, (2) the saturation magnetic moment per Fe atom, and (3) the Fe–Fe coordination numbers.

In the region of the low Si(Al) concentration the Fe–Fe ferromagnetic exchange interaction is predominant, which results in the increase of T_{C} with increasing Si(Al) content. With further increasing the Al concentration, other factors gradually show their influence on T_{C}, which decreases with the decrease of the saturation magnetic moment per Fe atom and the Fe–Fe coordination numbers.

Previous studies [4,5] have shown that in $NaZn_{13}$-type Fe-based intermetallic compounds the large entropy change should be related to its unusual magnetic phase transition and the drastic change of lattice parameter at T_{C}.

In the $LaFe_{11.3}Si_{1.1}Co_{0.6}$ compound, the thermomagnetic curve also shows an abrupt change at T_{C}, indicating the unusual magnetic phase transition. At the same temperature the negative lattice expansion also occurs. So there must be a close relation between them.

Now we focus our attention on the relation between the Fe–Fe bond length change and the unusual magnetic phase transition. In the $LaFe_{11.3}Si_{1.1}Co_{0.6}$ compound, we obtain the changes of Fe–Fe bond lengths before and after the phase transition, which are $\Delta h_{\mathrm{FeI--FeII}}$:-0.0010nm, Δh_A: 0.0002nm, Δh_B: -0.0013nm, Δh_C:-0.0018nm, Δh_D: 0.0001nm. Here h is Fe–Fe bond length. Ignoring other factors, we only consider how the change of Fe–Fe bond lengths affects the Fe–Fe exchange interaction. As the change of A and D bond lengths is only slight, their effect on the interaction can be neglected. In the volume of the eighth crystal lattice, we have $\Delta J_{\mathrm{tot}} = 4\Delta J_B - 2(\Delta J_{\mathrm{FeI--FeII}} + \Delta J_{\mathrm{C}})$. Because the B bond length is close to 0.255nm and the Fe^{I}–Fe^{II} and C bond lengths are close to 0.244nm, the change of the latter gives rise to a much faster change of Fe–Fe exchange interaction than that of the former. As $|\Delta h_{\mathrm{FeI--FeII}}|$, $|\Delta h_C|$ and $|\Delta h_B|$ have the same order of magnitude and have little difference, the following estimation has been made: $\Delta J_{\mathrm{tot}} = 4\Delta J_B - 2(\Delta J_{\mathrm{FeI--FeII}} + \Delta J_C) < 0$. In other words, if other factors are ignored, the change of Fe–Fe bond lengths gives rise to the decrease of the exchange interaction. Thus, it can be seen, in the thermomagnetic curve, that the magnetization change at T_{C} depends on two factors: (1) lattice vibration due to increasing temperature, (2) the decrease of exchange interaction due to the change of Fe–Fe bond lengths. As the magnetization change of common magnets only depends on the lattice vibration, a sharper change of magnetization occurs in $LaFe_{11.3}Si_{1.1}Co_{0.6}$ than in common magnets. Just based on this unusual magnetic phase transition, the $LaFe_{11.3}Si_{1.1}Co_{0.6}$ compound and the $NaZn_{13}$ type Fe-based intermetallic compounds exhibit the large magnetic entropy change.

With increasing Si concentration, the change of lattice parameter and Fe–Fe bond lengths before and after transition gradually decreases and the effect of them on the exchange interaction gradually vanishes. The transition also gradually changes from first-order to second-order.

In $LaFe_{12.4-x}Si_xCo_{0.6}$ (x=1.1, 1.7, 2.1) compounds, the effects of the substitution of Co and Si for Fe on magnetic entropy change and field-induced itinerant-electron metamagnetic (IEM) transition have been studied. It is shown that the substitution of a slight amount of Co for Fe weakens the first-order magnetic transition and drives T_C to a higher temperature. Though the magnetic transition is weakened, the magnetic entropy change still remains a considerable value and the higher T_C is advantageous to the research of magnetic entropy change near room temperature.

Since the IEM transition in the present compounds is related to the itinerant 3d electrons in Fe and Co, the substitution of Si for Fe leads to the gradual disappearance of the IEM transition. From the Arrott plots one can see that the compound $LaFe_{11.3}Si_{1.1}Co_{0.6}$ exhibits a clear IEM transition but the compound $LaFe_{10.7}Si_{1.7}Co_{0.6}$ exhibits only an inconspicuous one, while in compound $LaFe_{10.3}Si_{2.1}Co_{0.6}$ no evidence of IEM transition is observed.

From Maxwell's relation, the magnetic entropy change $\Delta S(T,H)$ is given by

$$\Delta S(T,H) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H, \qquad (1)$$

where H is the magnetic field, T is the sample temperature. Isothermal magnetization curves were measured in a magnetic field up to 5T, from which we obtain ΔS at different fields and different temperatures of $LaFe_{12.4-x}Si_xCo_{0.6}$ compounds for x=1.1,1.7 and 2.1 using Eq.(1). Figure 5 shows the plots of $|\Delta S|$ versus temperature under different magnetic field changes of 0–2T and 0–5T. The peak values of $|\Delta S|$ are 21.53, 11.78 and 6.93J/kg·K under the magnetic field change from 0 to 5T, and 13.20, 6.18 and 3.38J/kg·K under the magnetic field change from 0 to 2T for x=1.1,1.7 and 2.1 at their Curie temperatures which are 257.3K, 275.2K and 290.2K, respectively. The large ΔS should be related to the unusual magnetic phase transition and the drastic change of lattice parameter at T_C.

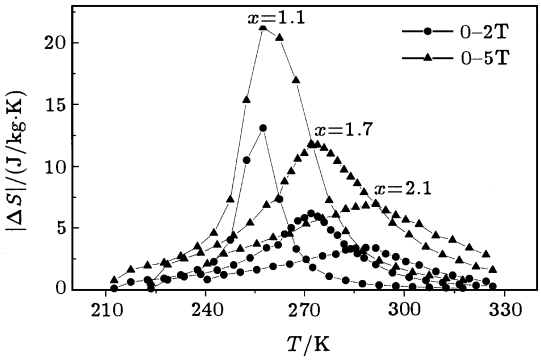


Fig.5. The entropy change $|\Delta S|$ as a function of temperature under different magnetic field change of 0–2T and 0–5T in $LaFe_{12.4-x}Si_xCo_{0.6}$ compounds.

The asymmetrical broadening of ΔS is also shown in Fig.5. It can be attributed to the field-induced IEM transition above T_C. In the $LaFe_{11.3}Si_{1.1}Co_{0.6}$ compound the critical field H_c of the IEM transition increases linearly with increasing temperature.[23] This leads to an additional contribution to magnetic entropy change above T_C according to Eq.(1), so ΔS is broadened at temperatures above T_C. If no IEM transition occurs as in the $LaFe_{10.3}Si_{2.1}Co_{0.6}$ compound, ΔS should be broadened at temperatures below T_C, based on the thermodynamic calculation for an ideal second-order ferromagnetic-to-paramagnetic transition.

4. Summary

The variation of Fe–Fe distances plays an important role in $NaZn_{13}$-type Fe-based intermetallic compounds. In $LaFe_{12.4-x}Si_xCo_{0.6}$ and $LaFe_{12.3-x}Al_xCo_{0.7}$ intermetallic compounds, the variation of Curie temperature and the unusual magnetic phase transition which results in the large entropy change can be explained by the analyses of Fe–Fe bond length change. In $LaFe_{12.4-x}Si_xCo_{0.6}$ compounds the effects of the substitution of Co and Si for Fe on the magnetic entropy change and field-induced IEM transition have also been studied and the maximum magnetic entropy change is 21.53J/kg·K under a magnetic field change from 0 to 5T at 257.3K for $LaFe_{11.3}Si_{1.1}Co_{0.6}$ compound.

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