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Magnetoresistances and magnetic entropy changes associated with negative lattice expansions in $NaZn_{13}$-type compounds LaFeCoSi*

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Magnetoresistances and magnetic entropy changes in $NaZn_{13}$-type compounds $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ (x=0.04, 0.06, and 0.08) with Curie temperatures of 243 K, 274 K, and 301 K, respectively, are studied. The ferromagnetic ordering is accompanied by a negative lattice expansion. Large magnetic entropy changes in a wide temperature range from ~230 K to ~320 K are achieved. Raising Co content increases the Curie temperature but weakens the magnetovolume effect, thereby causing a decrease in magnetic entropy change. These materials exhibit a metallic character below T_C, whereas the electrical resistance decreases abruptly and then recovers the metal-like behaviour above T_C. Application of a magnetic field retains the transitions via increasing the ferromagnetic ordering temperature. An isothermal increase in magnetic field leads to an increase in electrical resistance at temperatures near but above T_C, which is a consequence of the field-induced metamagnetic transition from a paramagnetic state to a ferromagnetic state.

Keywords: magnetoresistance, magnetic entropy change, negative lattice expansion, $NaZn_{13}$-type compounds
PACC: 7530S, 7550B, 6500

1. Introduction

The magnetocaloric effect (MCE) has been a topic of intense research in the past decades. The MCE is induced via the coupling of the magnetic sublattice with the magnetic field. It can be characterized by the isothermal entropy change ΔS, which can be easily obtained from magnetization measurements. The renewed interest in the MCE in recent years has arisen from the discovery of large magnetocaloric effects in some materials, such as $Gd_5Si_2Ge_2$,[1] FeRh,[2] $La(Fe,Si)_{13}$,[3] and MnFePAs[4] alloys. The origin of the MCE is found to be related to the simultaneous magnetic and structural phase transitions. In $Gd_5Si_2Ge_2$ alloys, the MCE has been observed at the temperature where the low-temperature ferromagnetic orthorhombic phase transforms into the high-temperature paramagnetic monoclinic phase.[1] In FeRh alloys, the ferro-antiferromagnetic phase transition accompanied by a large volume contraction without change in the crystal structure is responsible for the large MCE.[2] Both magnetic and structural transformations can lead to changes in both the charge carrier concentration and the scattering mechanisms. Considerable magnetoresistances have been observed in both $Gd_5Si_2Ge_2$ and FeRh alloys.[5,6]

It has been suggested recently that the compounds with cubic $NaZn_{13}$-type structure are appropriate magnetic refrigerant materials.[3,7−16] The large magnetic entropy change recently reported in this kind of ferromagnetic materials warrants its further exper-

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imental and theoretical studies. The achieved magnetic entropy change has been demonstrated to be due to a transition from a low-temperature ferromagnetic (FM) phase to a high-temperature paramagnetic (PM) phase, accompanied by a large lattice contraction. The simultaneous changes of magnetic order and phase volume should also cause changes in transport properties. However, there is little information on the electrical-transport properties of this kind of materials.

The $NaZn_{13}$-type compounds $LaFe_{13-x}Si_x$ with low Si contents show an itinerant electron metamagnetic transition above the Curie temperature T_C and a negative lattice expansion at T_C. With the decrease of Si content, the nature of the phase transition at T_C evolves from the second-order to the first-order, and the first-order nature is strengthened by further reducing the Si content. Furthermore, incorporation of Co weakens the first-order nature of the transition and drives T_C to a higher temperature. A proper combination of Si with Co could raise T_C up to near room temperature and preserve the first-order nature of the transition at T_C, characterized by a sharp change of lattice parameter. In this paper, we synthesize $NaZn_{13}$-type compounds $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ with x=0.04, 0.06, 0.08 and systematically investigate their magnetic entropy changes and magnetoresistances. T_C is tunable from 243 K to 301 K with Co doping from x=0.04 to 0.08. The influences of Co doping on the magnetic entropy change and magnetoresistance are discussed.

2. Experiment

The samples employed in the present investigation were prepared by repeatedly arc-melting an appropriate number of the starting materials in high-purity (99.996%) argon atmosphere with a background pressure of 10^{-4} Pa. The commercial purities of La, Fe, Co, Si are 99.9wt%, 99.99 wt%, 99.9 wt%, and 99.999 wt%, respectively. The ingots each were wrapped with Ta foil and subsequently homogenized in a sealed quartz tube with a high vacuum of 10^{-4}Pa at 1323 K for 30 days, then quenched in liquid nitrogen. The influence of oxygen should be neglectable, particularly for the central parts of the ingots. The samples for measurement are cut from the central parts of each ingot. It is worthy to point out that quenching is important to obtain a stable compound with a low Si content for this kind of alloys. The fraction of Si content involved in present samples $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ (x=0.04, 0.06, 0.08) is the limit that can be reached by using such a synthesizing method. Further reducing Si content would cause the appearance of a large quantity of α-Fe impurities in the compounds. X-ray diffraction analysis confirmed the single phase of the $NaZn_{13}$-type structure existing in present samples. A minor phase α-Fe was observed. The fraction of the impurity α-Fe phase was estimated to be 4–6wt% based on the chemical analysis by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). Within the sensitivity $\pm$0.01 wt%, no other elements were detected. We believe that the interstitial impurities, such as C, N, O, H, or F, should be too small in quantity to play a role in the formation of the present $NaZn_{13}$-type compounds, if any, during the preparation of the materials. The quantity of α-Fe impurities might vary slightly from sample to sample in different parts of the same ingot. All magnetic measurements were performed using a superconducting quantum interference device (SQUID) magnetometer. The values of Curie temperature T_C were determined to be 243 K, 274 K, and 301 K for samples $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ (x=0.04, 0.06, 0.08) from the temperature-dependent magnetization measured under a field of 0.01 T. The samples used for electrical resistance measurements were cut from the main samples by spark erosion and had the dimensions 2 × 2 ×5mm^3. The electrical resistance measurements were performed using SQUID equipped with a probe for making four-point electrical resistance measurements. The measurements were carried out at a current of 10 mA in a temperature range from 5 K to 380 K and under magnetic fields from 0 to 4 T.

3. Results and discussion

X-ray powder diffraction (XRD) at various temperatures was performed for all samples in order to study the structure change when the magnetic state varied with temperature. It was found that the crystal structure retained cubic $NaZn_{13}$-type, but the lattice parameter changed dramatically at T_C, implying a first-order transition. Figure 1 shows the temperature dependence of lattice parameter obtained from the XRD spectra. The large negative thermal expansion appears near T_C. The lattice parameters in the ferromagnetic state for different samples x=0.04, 0.06, and 0.08 are $\sim$ 0.63%, 0.44%, and 0.41% bigger than those in the paramagnetic state, respectively, in the vicinity of T_C. The substitution of Co for Fe atoms can influence the magnetovolume ef-

fect. The extent of lattice contraction decreases gradually with the increase of Co doping. Measurements of ac susceptibility to heating and cooling indicate that temperature hystereses of the transitions for all samples are small, < 2 K. In the past, several theories have been used to describe magneto–elastic effects in itinerant magnetic systems.[17–19] A widely used theory is the local-moment volume magnetostriction, in which the magnetovolume effect arises from the volume dependence of the exchange integral between spins. A theory developed by applying the Stoner band model suggests that the magnetovolume effect is related to the increase in kinetic energy of the electron system due to the splitting of the 3d band. For LaFeAl compounds with a $NaZn_{13}$-type structure, previous investigations[17] indicated that the magnetovolume effect originated from both the local-moment and band part, but the latter contributed much more than the former. For the better understanding of the origin of the large negative expansion near T_C in present compounds, detailed information about the band structure is still needed.

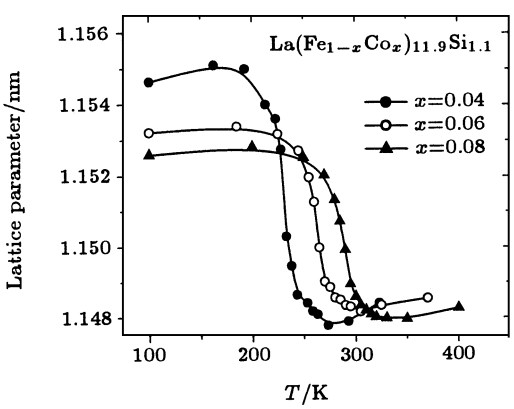


Fig.1. The temperature dependent lattice parameter of $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ (x=0.04, 0.06, 0.08) compounds.

Figure 2 displays the magnetization isotherms of $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ (x=0.04, 0.06, 0.08) measured in a wide temperature range as the magnetic field increases and decreases. One can find that the magnetic hystereses, with the field varied, are small for all samples. Moreover, the substitution of Co for Fe atoms further reduces the magnetic hysteresis. The maximal area of the field hysteresis near T_C for the x=0.04 sample is $\sim$119kT·A·m^{-1}. which decreases to about 52kT·A·m^{-1} for x=0.06 and 0.08 samples. The small field hysteresis is considered to be a characteristic favourable for magnetic refrigeration applications.

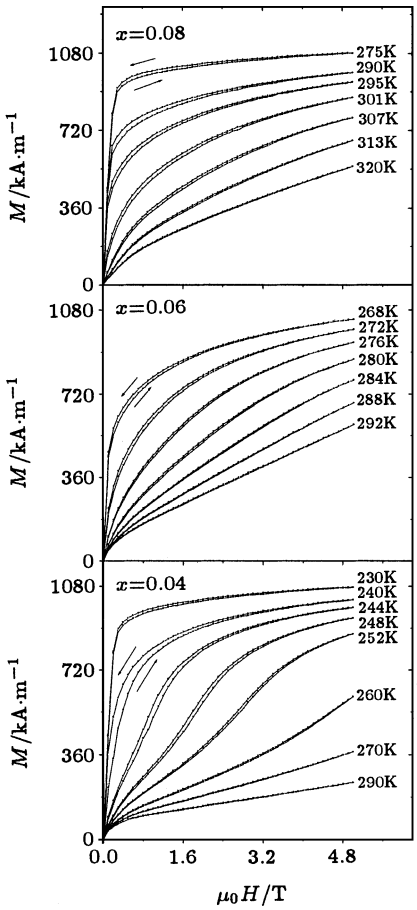


Fig.2. Magnetization isotherms of $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ (x=0.04, 0.06, 0.08) compounds. (a) Isotherms as the field increases. Temperature step is 2K in the vicinity of T_C, and 5K for the regions away from T_C. (b) Selected isotherms measured as the field increases and decreases.

Figure 3 shows the magnetic entropy change ΔS as a function of temperature and magnetic field, obtained by using Maxwell relation $\Delta S(T,H) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H$.[1,3,4,20] The ΔS of Gd is also presented for comparison. One can find that the $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$compounds show large ΔS in a wide temperature range from $\sim$230 K to $\sim$320 K. The ΔS significantly exceeds that of Gd. The ΔS in magnitude decreases with the increase of Co doping, which is correlated with the weakening of the magnetovolume effect (see Fig.1). The weakening of magnetovolume effect would lead to a reduction in the slope of $M-T$ curve near T_C, and thus a decrease in ΔS according to Maxwell relation.

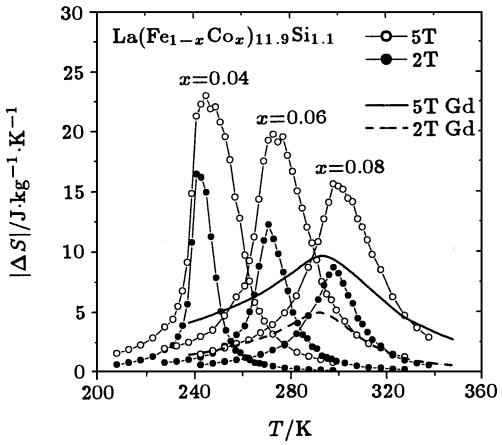


Fig.3. Magnetic entropy change $|\Delta S|$ of $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ (x=0.04, 0.06, 0.08) in comparison with that of Gd for the magnetic field changing from 0 to 2, and 0 to 5T.

The asymmetrical broadening of ΔS peak with the field increasing for $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ is also observed, which is a consequence of the field-induced itinerant-electron metamagnetic (IEM) transition from the paramagnetic state to the ferromagnetic state above T_C.[3] Increasing Co content makes the phenomenon of asymmetrical broadening weak. It seems that the substitution of the Co for Fe atoms can suppress the IEM transition in the present compounds. The phenomenon of the IEM transition was historically observed in many d electron systems. Yamada discussed it by taking into account the effect of spin fluctuations on the Ginzburg–Landau theory.[21] The field-induced IEM transition is closely related to the double minima of the paramagnetic state and the ferromagnetic state in the magnetic-free energy as a function of magnetization. The applied fields cause the energy minimum of the ferromagnetic state to be lower than that of the paramagnetic state above T_C, resulting in the IEM transition. Generally, the IEM transition is related to a particular d electron band structure which exhibits a sharp peak of the density of states (DOS) just below the Fermi level.[21] It is known that the IEM transition in Laves phase compounds is attributed to a unique Co 3d band structure.[21,22] Unfortunately, no information on the band structure is available for present compounds. Their IEM transition may be influenced by not only the electronic structure but also the elastic energy change.[21−23] A reduction in the elastic energy change with Co doping (see Fig.1) may be a possible reason for the gradually weakening of the IEM transition with Co content increasing.

We choose two (x=0.04, 0.06) of the present samples for resistance measurements, with their more pronounced magnetovolume effects considered. The temperature-dependent electrical resistances measured in the zero and 4T fields in a cooling process are presented in Fig.4. It can be seen that there is an anomaly in the temperature dependence of the electrical resistance at T_C in the absence of magnetic field. Below T_C, the electrical resistance increases with the increase of temperature, showing a metallic character, but above T_C, it decreases dramatically in a narrow temperature range and then recovers the metal-like dependence on temperature. The low residual resistance ratio might be related to the existence of α-Fe impurity.

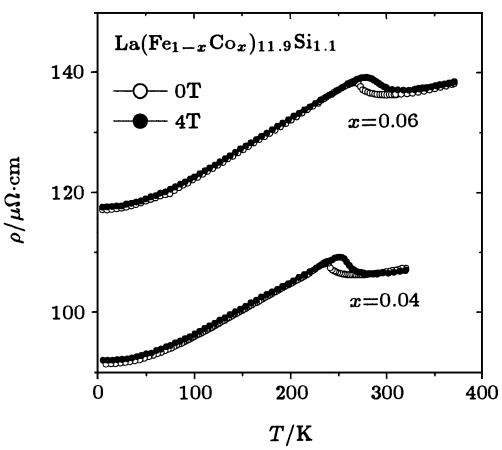


Fig.4. The temperature dependence of electrical resistance measured in a zero and 4T field for the cooled $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ (x=0.04, 0.06) compounds.

It is noteworthy that in our samples the total contribution from both the electron–phonon scattering and the electron–magnon scattering in the PM phase is smaller than that in the FM phase, which is contrary to normal FM metallic materials and also much different from other systems showing giant magnetocaloric effect, such as $Gd_5Si_2Ge_2$ alloy.[5] The giant magnetocaloric effect in $Gd_5Si_2Ge_2$ comes from the simultaneous magnetic and structural transitions from a low-temperature FM orthorhombic phase to a high-temperature PM monoclinic phase.[1] The monoclinic PM phase in $Gd_5Si_2Ge_2$ shows a higher resistance than the orthorhombic FM phase.[5] It has been argued that the change in the electron–phonon scattering during the transition is the primary mechanism responsible for the resistance increasing in the PM monoclinic phase. The monoclinic lattice of PM phase is more disordered than the orthorhombic lattice of FM phase, resulting in the increase in electron–phonon scattering. It is generally believed that the

most important contribution to the electrical resistivity during the first-order magnetic and crystallographic phase transitions results from the electron–phonon scattering and the electron–magnon scattering. In most FM metallic materials, the electron–magnon component usually approaches maximum at T_C and then becomes weakly dependent on temperature above T_C. In $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ (x=0.04, 0.06, 0.08) compounds, magnetic phase transition at T_C is accompanied by a large change of lattice parameter of the same $NaZn_{13}$-type structure. It is naturally considered that the change of electron–phonon scattering, when the phase transition takes place, might be responsible for the reduction in resistance in the PM phase of $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$. The large change of the lattice parameter may influence the density of states at the Fermi level and affect the electron–phonon scattering, besides the direct influence on the carrier concentration. A quantitative explanation for the resistance decreasing in PM phase with lattices shrinking still requires detailed information about the band structure. One can also find from Fig.4 that the slope of resistance curve, dR/dT, near T_C for the sample x=0.06 is smaller than that for x=0.04, which should be related to a reduction in elastic energy change with the increase of the substitution of Co for Fe atoms.

The application of a magnetic field retains the transition via increasing the ferromagnetic ordering temperature (see Fig.4). The transition temperature increases from 274 K to 294 K for the sample x=0.06 and from 243 K to 265 K for the sample x=0.04 with a field of 4T applied. The resistance at temperatures away from T_C is kept nearly unchanged when a field of 4T is applied. However, at the temperatures near but above T_C, application of magnetic field does result in an increase in resistance.

The isothermal magnetic-field-dependent resistances measured at temperatures near T_C for the sample x=0.06 as the field increases and decreases are shown in Fig.5. It can be found that the isothermal increase in magnetic field leads to an increase in electrical resistance at temperatures close to but above T_C. This is a consequence of the field-induced IEM transition from the paramagnetic (PM) state to ferromagnetic (FM) state.[3] The field hysteresis of the transition in the field cycles is small in present systems, which is consistent with the small temperature hysteresis.

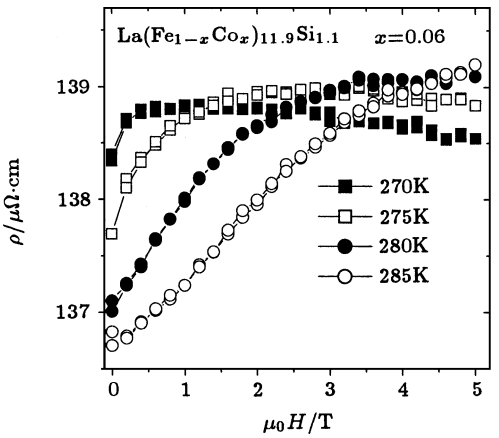


Fig.5. The isothermal magnetic-field dependence of electrical resistance of $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ (x=0.06) compounds at temperatures 270 K, 275 K, 280 K, and 285 K, respectively, as the field increases and decreases.

4. Summary

The $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ (x=0.04, 0.06, 0.08) compounds with the Si content reaching the lowest limit and tunable T_C from 243 K to 301 K are successfully synthesized using the present synthesis method. The magnetic ordering at T_C is accompanied by a large increase in lattice parameter without changing the $NaZn_{13}$-type structure. Large magnetic entropy change in a wide temperature range from ~230 K to ~320 K is achieved, which is ascribed to the simultaneous magnetic order and lattice volume change. The substitution of Co for Fe increases T_C but reduces the extent of lattice contraction and suppresses the IEM transition gradually, thereby leading to a decrease in ΔS and the weakening of the asymmetrical broadening of the ΔS peak. The temperature and field dependences of the electrical resistance also indicate that the transition at T_C can be induced by both temperature and magnetic field. The change of electron–phonon scattering during the transition may be the main reason for the resistance decreasing in PM phase. The magnetic-field-induced itinerant-electron metamagnetic transition (IEM) from a PM to FM state leads to a positive magnetoresistance at temperatures close to but above T_C.

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