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Strong interplay between structure and magnetism in the giant magnetocaloric intermetallic compound $\text{LaFe}_{11.4}\text{Si}_{1.6}$: a neutron diffraction study

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Abstract

Crystallographic and magnetic structures of the cubic NaZn_{13} -type intermetallic compound $\text{LaFe}_{11.4}\text{Si}_{1.6}$ have been studied by means of powder neutron diffraction. Rietveld analysis indicates that Si atoms substitute for Fe atoms randomly on two different Fe sites. All spins in the unit cell are aligned ferromagnetically with the Fe^{I} (8b) moment smaller than the Fe^{II} (96i) one. The long-range ferromagnetic ordering induces a drastic expansion of the lattice and the coexistence of the large and small volume phases near the Curie temperature. Even in the ferromagnetic state, the lattice expansion still correlates strongly with the spontaneous magnetic moment, marked by a large positive magnetovolume coupling constant $kC = 1.14 \times 10^{-8} \text{ cm}^6 \text{ emu}^{-2}$. From the temperature dependence of Fe–Fe bond lengths, we suggest that the Fe–Fe exchange interaction between the clusters (each formed by a central Fe^{I} atom and 12 surrounding Fe^{II} atoms) plays an important role in the magnetic properties of $\text{La}(\text{Fe}_{1-x}\text{Al}/\text{Si}_x)_{13}$, as does that within the clusters.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The magnetocaloric effect (MCE) is one of the fundamental physical phenomena in magnetic materials, which maps out the magnetic phase transition induced by the temperature and magnetic field. Those materials with large MCE also have a potential application as effective refrigerants [1, 2]. Compared with the convenient gas refrigerants, magnetic refrigerants have the advantages of high efficiency of energy transformation and environmental protection. Refrigerators working near room temperature with magnetic refrigerants are highly desirable because they would be very suitable for use in our daily lives, for example in food cooling,

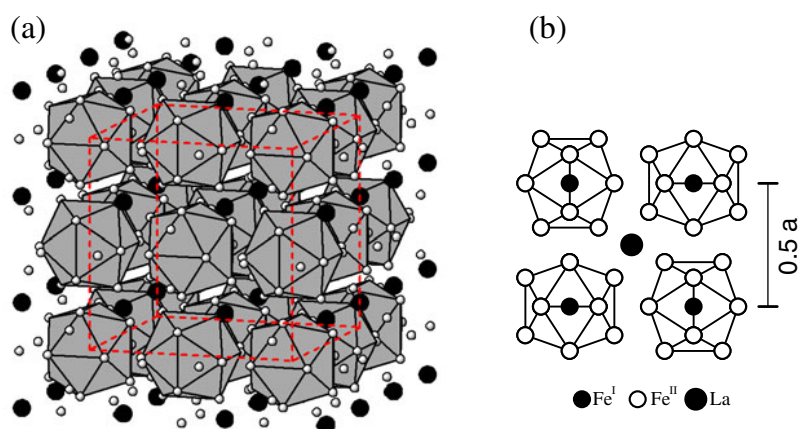


Figure 1. (a) The cubic NaZn_{13} -type structure of hypothetical LaFe_{13} . It should be noted that each cluster is formed by one central Fe^{I} atom and its nearest neighbours of 12 Fe^{II} atoms, where the Fe^{I} atom enclosed by an icosahedron of 12 Fe^{II} atoms is not displayed. (b) The (001) projection of a part of the unit cell.

air conditioning, etc. Although no working magnetic refrigerator exists today, a great deal of research on looking for large MCE materials has been reported. Recently, the giant near-room-temperature MCE induced by first-order magnetic phase transitions has attracted extensive attention. Three types of materials have been found: (1) Gd-based alloys $\text{Gd}_5(\text{Si}, \text{Ge})_4$ [3–5], (2) transition-metal-based phosphide–arsenides $\text{MnFe}(\text{P}, \text{As})$ [6] and (3) Fe-based rare-earth transition-metal intermetallic compounds $\text{La}(\text{Fe}, \text{Co}, \text{Al/Si})_{13}$ [7–9]. Compared with the broad λ -like peak of magnetic entropy change $\Delta S_{\text{M}}(T)$, induced by the second-order magnetic phase transition, the widths of the $\Delta S_{\text{M}}(T)$ peak in these new giant MCE materials are quite narrow and the maximum value is much higher. The peak values of ΔS_{M} for magnetic field changes from 0 to 5 T, derived from the data of the isothermal magnetization measurement, are $19 \text{ J kg}^{-1} \text{ K}^{-1}$ for $\text{Gd}_5\text{Si}_2\text{Ge}_2$ at 277 K [3], $18 \text{ J kg}^{-1} \text{ K}^{-1}$ for $\text{MnFe}(\text{P}_{0.45}\text{As}_{0.55})$ at 310 K [6] and $20.3 \text{ J kg}^{-1} \text{ K}^{-1}$ for $\text{La}(\text{Fe}_{11.2}\text{Co}_{0.7}\text{Si}_{1.1})$ at 274 K [7]. All of these values are nearly twice those of the $\Delta S_{\text{M}} \sim 9.80 \text{ J kg}^{-1} \text{ K}^{-1}$ for Gd (at 293 K), a typical near-room-temperature large MCE material induced by the second-order phase transition.

The pseudo-binary intermetallic compounds $\text{La}(\text{Fe}, \text{Co}, \text{Al/Si})_{13}$ crystallize into the cubic NaZn_{13} -type structure (space group: $Fm\bar{3}c$) by substituting Al [8–10] or Si [7, 11, 12] for part of the Fe although the binary intermetallic LaFe_{13} does not exist. As seen in figure 1, in the hypothetical LaFe_{13} the Fe atoms are located at two different symmetric sites, Fe^{I} at 8b (0, 0, 0) and Fe^{II} at 96i(0, y, z), in a ratio of 1:12. La atoms at 8a(1/4, 1/4, 1/4) are surrounded by 24 Fe^{II} atoms. One central Fe^{I} atom and its nearest neighbours of 12 Fe^{II} atoms form a cluster. Besides the giant MCE, strong critical behaviour and different magnetic transitions, such as ferromagnetic, antiferromagnetic and metamagnetic, were also reported in $\text{La}(\text{Fe}_{1-x}\text{Al/Si}_x)_{13}$ [7–12]. In the present study, we study the crystallographic and magnetic structures of $\text{LaFe}_{11.4}\text{Si}_{1.6}$ by high-resolution neutron powder diffraction. Random distribution of Si atoms and strong interplay between the lattice and magnetism are observed. The relationship between Fe–Fe bond lengths and magnetic properties is discussed in detail.

2. Experiment

The $\text{LaFe}_{11.6}\text{Si}_{1.4}$ sample was prepared by arc melting in an atmosphere of ultra-pure argon gas. The purities of the starting elements were better than 99.9%. The sample was subsequently

annealed in an evacuated quartz tube for one month at 1273 K. The Curie temperature $T_C = 293$ K was derived from the temperature dependence of magnetization recorded by a SQUID magnetometer (Quantum Design). Neutron diffraction was carried out on a powder sample in the temperature range 2–300 K on the diffractometer G4.2 [13], installed on the cold neutron guide at the reactor ORPHEE of the Laboratoire Leon Brillouin, France. The incident beam was focused by a Ge monochromator with a wavelength $\lambda = 2.3433$ Å. Data collected over the range $2\theta = 6^\circ$ – 140° with a step increment of 0.1° were analysed by the Rietveld technique via the program FULLPROF [14]. The scaling factor, background, peak shape, atomic positions, thermal vibration factor, occupancies ($T > T_C$) and magnetic moments ($T < T_C$) were determined.

3. Results and discussion

Powder diffraction patterns confirm that the annealed sample crystallizes in the cubic NaZn_{13} -type structure (space group: $Fm\bar{3}c$) over the whole range of temperature (2–300 K) with $\sim 5\%$ of α -Fe as a secondary phase. The Si occupancies were determined by refining the diffraction patterns collected at high temperatures ($T > T_C$). Rietveld refinements show the occupancy of Fe atoms are $\sim 90.5(\pm 1.7)$ and $\sim 87.0(\pm 1.8)\%$ for Fe^{I} and Fe^{II} sites, respectively. Thus Si atoms are almost randomly distributed on these two Fe sites and the determined Si concentration of $1.6(\pm 0.3)$ coincides with the starting stoichiometric ratio. One can see that the pattern determined at 300 K in figure 2(a) is statistically in agreement with the observed data.

Generally, the positive heat of alloying between La and Fe is considered to be the reason why no La–Fe binary compound exists [15]. In order to lower the heat of formation effectively, the substituting atoms, such as Al and Si, are therefore expected to preferentially occupy Fe^{II} sites which are the nearest neighbours of La. This expected preferential occupation at Fe^{II} sites, in agreement with the case in $\text{La}(\text{Fe}_{1-x}\text{Al}_x)_{13}$ [16, 17], is apparently in conflict with our observed random distribution of Si atoms. In previous work [10, 11], the linear drop of Fe magnetic moments with increasing Si/Al concentration seems to imply electronic transfer between the Fe and Si/Al atoms, which thus gives rise to an energy band change. Consequently, the random Si distribution perhaps suggests that, except for lowering the heat of formation, the band change could play another important role in stabilizing the NaZn_{13} -type pseudo-binary compounds $\text{La}(\text{Fe}_{1-x}\text{Al/Si}_x)_{13}$.

The spin configuration was determined by refining the neutron diffraction patterns collected at low temperatures ($T < T_C$) with fixed Si occupancies. The fact there are no additional superlattice reflections implies ferromagnetic ordering, in agreement with the magnetic measurements. As an example, figure 2(c) illustrates that the pattern collected at 2 K fitted the ferromagnetic spin configuration very well. The refined moment values (table 1) increase from $\mu(\text{Fe}^{\text{I}}) = 1.3(1) \mu_B$, $\mu(\text{Fe}^{\text{II}}) = 1.70(6) \mu_B$ at 185 K up to $1.54(9) \mu_B$, $2.16(5) \mu_B$ at 2 K, respectively. Obviously, the Fe^{II} moment is nearly one-third larger than the Fe^{I} one, as observed in ferromagnetic $\text{La}(\text{Fe}_{1-x}\text{Al}_x)_{13}$ by neutron diffraction [16, 17]. Since the Fe^{I} atoms are surrounded by 12 Fe^{II} atoms, one can suggest a face-centred-cubic (fcc) lattice environment for the Fe^{I} atoms. So the small Fe^{I} moment may consequently be interpreted in terms of the instability of Fe magnetism in the fcc lattice, as with γ -Fe, suggested by band calculation [18, 19].

It is noted that the diffraction profile of 191 K (very close to the Curie temperature) must be fitted by two cubic NaZn_{13} -type lattices with different lattice parameters (figure 2(b)). This characteristic is clearly displayed in figure 3 where the (820), (644) and (660) reflections have been indicated at the temperatures near the Curie temperature. No difference is observed between the diffraction profiles at 185 and 193 K except for significant shifts of the peak

Table 1. Structural data of LaFe_{11.4}Si_{1.6} and magnetic moments of Fe atoms from the Rietveld analysis of the profile data collected at seven selected temperatures.

	300 K	250 K	193 K	185 K	100 K	50 K	2 K
a (Å)	11.4782(1)	11.4735(1)	11.4786(1)	11.5259(1)	11.5317(1)	11.5327(1)	11.5328(1)
B _{overall} (Å ²)	1.03(4)	1.08(4)	0.75(4)	0.58(3)	0.52(3)	0.51(3)	0.21(4)
Fe ^{II} (0, y, z)							
y	0.179 25(7)	0.179 29(6)	0.179 41(7)	0.179 66(7)	0.179 80(6)	0.179 89(7)	0.179 80(7)
z	0.116 68(7)	0.116 78(7)	0.116 83(7)	0.116 13(7)	0.116 06(6)	0.115 99(7)	0.115 95(7)
μ[Fe ^I] (μ _B)				1.3(1)	1.51(9)	1.59(9)	1.54(9)
μ[Fe ^{II}] (μ _B)				1.70(6)	2.04(5)	2.12(4)	2.16(5)
R _{wp} (%)/χ ²	7.65/3.32	7.45/3.13	7.85/3.57	8.48/4.00	7.94/3.56	8.38/4.18	8.83/4.05
R _{Bragg} /R _m (%)	2.36/—	2.97/—	2.32/—	3.18/4.63	2.60/4.72	2.89/5.07	2.48/4.18
Bond lengths (Å):							
La–Fe ^{II} (24)	3.3519(7)	3.3499(4)	3.3508(4)	3.3676(4)	3.3693(4)	3.3698(4)	3.3702(4)
Fe ^I –Fe ^{II} (12)	2.4550(7)	2.4550(7)	2.4575(8)	2.4657(8)	2.4678(8)	2.4685(8)	2.4674(8)
Fe ^{II} –Fe ^{II} :B1(1)	2.678(1)	2.679(1)	2.678(1)	2.682(1)	2.677(1)	2.675(1)	2.674(1)
B2(4)	2.5579(7)	2.5576(6)	2.5604(7)	2.5721(9)	2.5749(7)	2.5761(7)	2.5750(7)
B3(2)	2.4951(9)	2.4947(9)	2.4945(9)	2.4925(9)	2.4908(9)	2.4887(9)	2.4895(9)
B4(2)	2.450(1)	2.447(1)	2.448(1)	2.465(1)	2.466(1)	2.467(1)	2.468(1)

positions. The profile at 191 K can be obtained by summing the above two patterns with different scales. The onset of the ferromagnetic ordering results in a large volume expansion, but has no influence on the symmetry of the atomic lattice. The volume changes discontinuously and the large volume ferromagnetic phase coexists with the small volume paramagnetic phase at 191 K. The refinement shows that, at 191 K, the sample consists of ~12% of the large volume phase and ~83% of the small one (besides ~5% α-Fe). This coexistence implies the first-order magnetic phase transition and strong interplay between lattice and magnetism, in agreement with the observation in La(Fe_{0.88}Si_{0.12})₁₃ by x-ray diffraction [12]. Regrettably, we cannot determine the Fe moments here because of the low concentration of the large volume ferromagnetic phase.

The large lattice expansion induced by ferromagnetic ordering can also be seen in figure 4, where the lattice parameter and Fe atomic moments are shown as a function of temperature. It can be seen that the lattice parameter is strongly correlated with the Fe moment. With decreasing temperature, from 300 to 250 K, the compound seems to display a normal thermal contraction resulting from the anharmonic vibrations of atoms. The linear thermal expansion coefficient $\alpha_t \sim 6 \times 10^{-5} \text{ K}^{-1}$ is consistent with that in the common metals, but larger than that in La(Fe_{1-x}Al_x)₁₃ ($\alpha_t \sim 1.3 \times 10^{-5} \text{ K}^{-1}$) measured by a three-terminal capacitance technique [10]. For the temperature range of 250–210 K, $\alpha_t \sim 1 \times 10^{-6} \text{ K}^{-1}$, indicating Invar behaviour as observed in La(Fe_{1-x}Al_x)₁₃ [10]. Since the Invar effect is caused by the expansion resulting from the spontaneous magnetostriction which cancels the normal thermal contraction, one may infer that the short-range magnetic correlation has appeared far above the Curie temperature in LaFe_{11.4}Si_{1.6}. With a further reduction in temperature, the effect of the spontaneous magnetostriction increases and the lattice parameter shows a large jump with long-range ferromagnetic ordering. Even below the Curie temperature, the contribution of magnetic thermal expansion is still related to the increase of the magnetic correlation as the temperature is lowered.

Theoretically, in a strongly, or intermediately, correlated ferromagnetic system, the spontaneous volume magnetostriction ω_s can be written as [20]

$$\omega_s = \omega_s^{\text{band}} + \omega_s^{\text{int}}$$

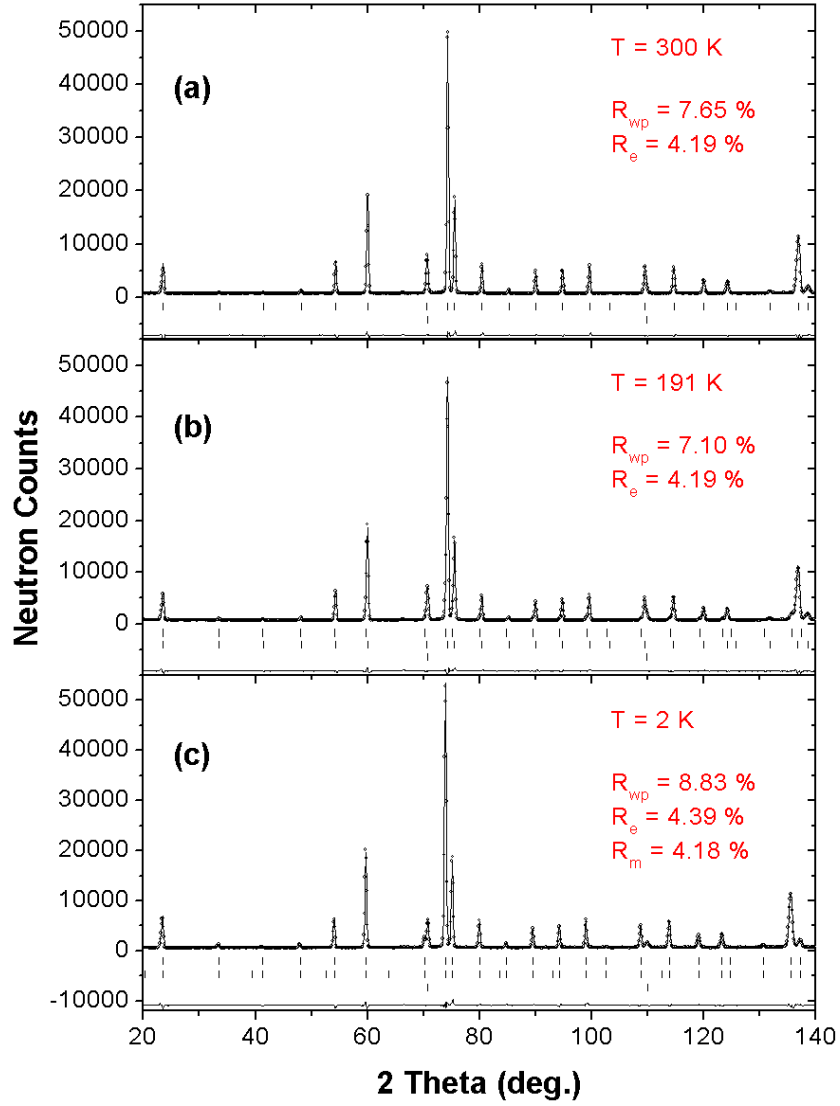


Figure 2. Observed (dot) and calculated (line) neutron diffraction patterns and their difference for LaFe_{11.4}Si_{1.6} at (a) $T = 300$ K, (b) $T = 191$ K and (c) $T = 2$ K.

where $\omega_s^{\text{band}} = kC^{\text{band}} \sum_i m_i^2(T)$ is the contribution from the energy band part and $\omega_s^{\text{int}} = kC^{\text{int}} \sum_{i,j} \langle m_i(T) \cdot m_j(T) \rangle$ is the contribution from the local exchange interaction. Here, k is the compressibility, $m(T)$ the temperature-dependent local moment and C^{band} and C^{int} are the magnetic volume coupling constants due to the band and local exchange mechanisms, respectively. Below the Curie temperature, $\langle m_i(T) \cdot m_j(T) \rangle$ and $m_i^2(T)$ can be approximated by spontaneous magnetization $M^2(T)$. This leads to the relation

$$\omega_s = k(C^{\text{band}} + C^{\text{int}})M^2(T).$$

As seen in figure 5, the spontaneous volume magnetostriction ω_s , extracted from the lattice change with $\omega_s = \Delta V/V = 3\Delta l/l$, linearly depends on $M^2(T)$. Note that the linear

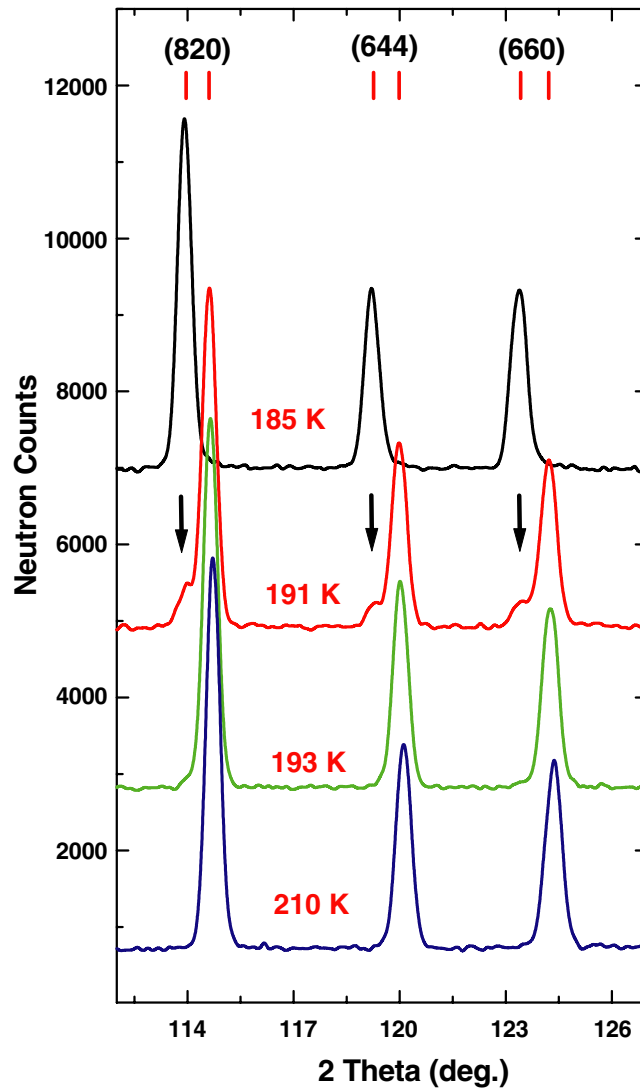


Figure 3. The profiles of reflections of (820), (644) and (660) with the temperature crossing the Curie temperature. The coexistence of the large (indicated by arrows) and small volume phases at 191 K, induced by the long-range ferromagnetic ordering is clearly displayed.

normal thermal effect, defined by the high-temperature slope of $\Delta l/l$, has been subtracted here. Thus a large positive magnetovolume coupling constant $kC = k(C^{\text{band}} + C^{\text{int}}) = 1.14 \times 10^{-8} \text{ cm}^6 \text{ emu}^{-2}$, very close to $1.4 \times 10^{-8} \text{ cm}^6 \text{ emu}^{-2}$ in the FeNi-Invar alloys [20], but much less than that in $\text{La}(\text{Fe}_{1-x}\text{Al}_x)_{13}$ [10]. Furthermore, $\omega_s(T \sim 0 \text{ K}) = 1.8\%$, seen in the inset of figure 5, also satisfactorily agrees with 1.9% in the FeNi-Invar alloys [20].

Figure 6 displays the bond lengths as a function of temperature in $\text{LaFe}_{11.4}\text{Si}_{1.6}$. The normal thermal expansion has no apparent effect on the bond lengths as usual, so the bond lengths just have a slight change in paramagnetic state or ferromagnetic state. However, the first-order ferromagnetic ordering induces a large jump for most of them with lowering the temperature below T_C . Bond lengths of La-Fe^{II} and $\text{Fe}^{\text{I}}\text{-Fe}^{\text{II}}$ increase by $\sim 0.5\%$ as the lattice

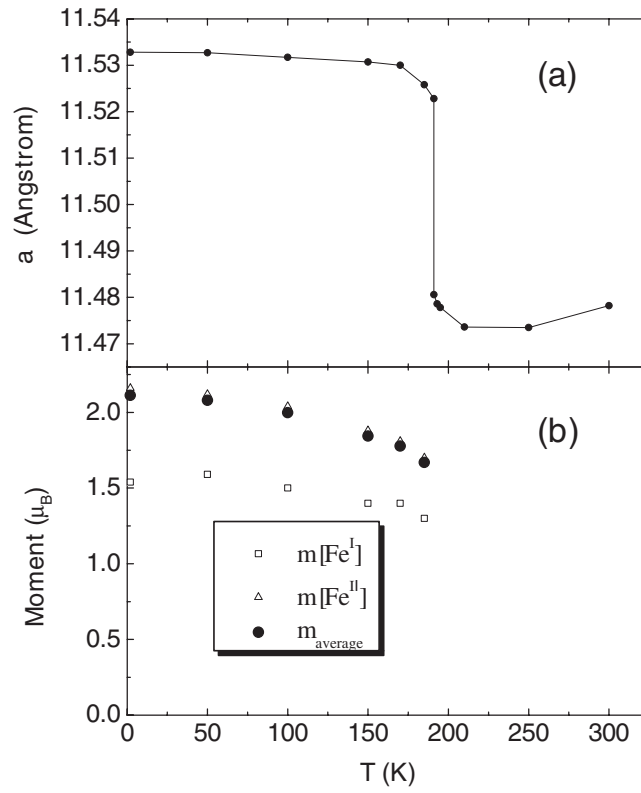


Figure 4. Lattice parameter (a) and magnetic moments per Fe atom (b) as a function of temperature extracted from the final refinements.

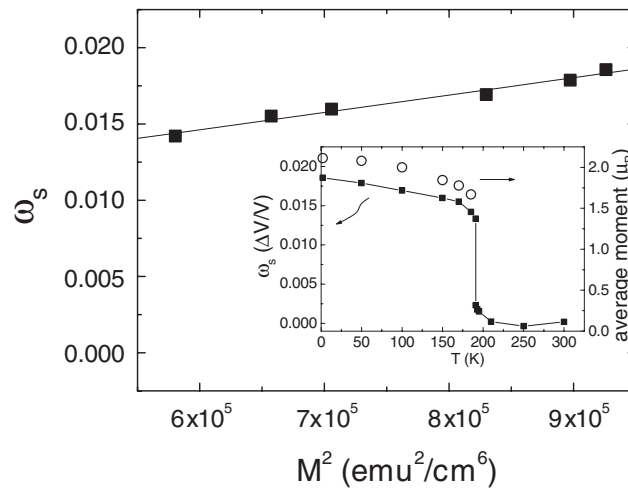


Figure 5. Spontaneous volume magnetostriction ω_s as a function of squared magnetization M^2 in $\text{LaFe}_{11.4}\text{Si}_{1.6}$. The inset shows the temperature dependence of ω_s together with the average magnetic moment per Fe atom.

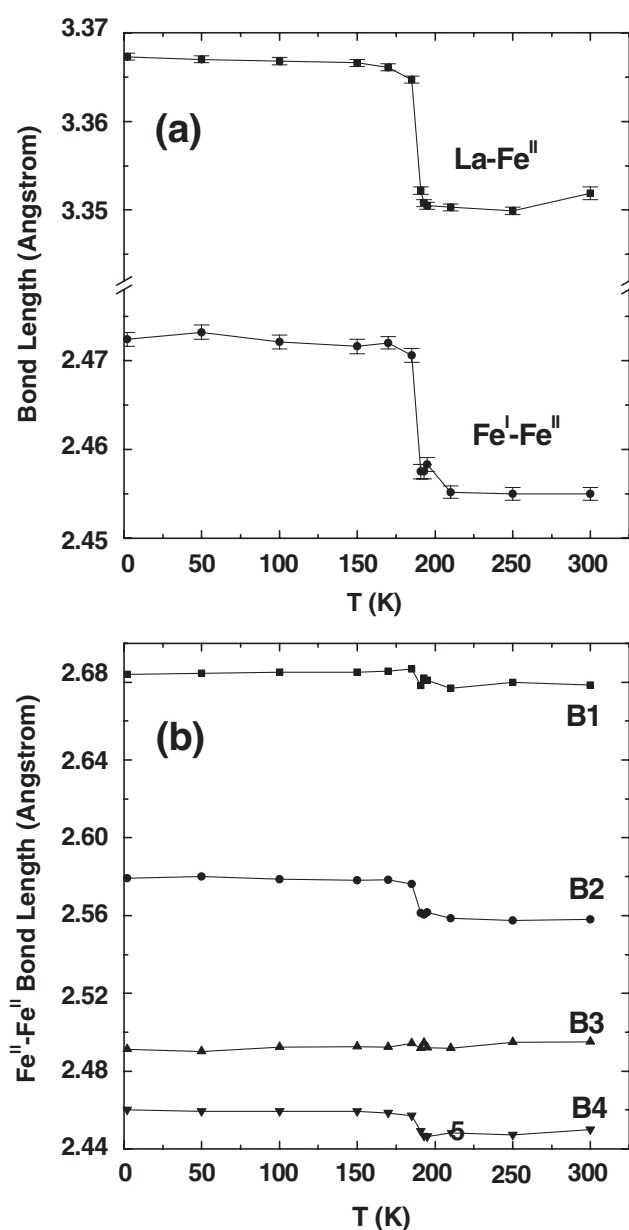


Figure 6. Bond lengths in $\text{LaFe}_{11.4}\text{Si}_{1.6}$: (a) La-Fe^{II} and Fe^I-Fe^{II}, (b) Fe^{II}-Fe^{II}. It should be noted that the intra-cluster Fe^{II}-Fe^{II} bond lengths are marked by B1 and B2 while the inter-cluster ones are marked with B3 and B4.

constant increases (figure 6(a)). If classifying the Fe^{II}-Fe^{II} bond lengths into two types: the intra-cluster (B1, B2) and the inter-cluster (B3, B4) ones, seen in figure 6(b) one can see that, interestingly, the inter-cluster bond lengths are much smaller than the intra-cluster ones. In more detail, the relatively longer bonds in each type are lengthened a little ($<0.2\%$ for B1, almost constant for B3) while the shorter ones (B2, B4) lengthen by $\sim 0.5\%$. It maybe

implies that the ferromagnetism in $\text{La}(\text{Fe}_{1-x}\text{Si}_x)_{13}$ prefers the longer $\text{Fe}^{\text{II}}\text{--Fe}^{\text{II}}$ bond lengths rather than the shorter ones. Usually, dense-packed Fe-based alloys are weak ferromagnets with a pronounced tendency towards antiferromagnetic exchange interaction at small Fe–Fe distances [21]. Therefore, the increase of the Curie temperatures in $\text{La}(\text{Fe}_{1-x}\text{Al}_x)_{13}\text{N}_3$ due to the absorption of nitrogen can be interpreted by a strengthened Fe–Fe magnetic interaction with those interstitial nitrogen atoms that are located between the icosahedron clusters to significantly lengthen the short inter-cluster $\text{Fe}^{\text{II}}\text{--Fe}^{\text{II}}$ bonds [22]. Also we guess that the large increase of T_C due to the absorption of hydrogen [23, 24] in $\text{La}(\text{Fe}_{1-x}\text{Si}_x)_{13}\text{H}_y$ seems to have the same origin. In other words, the inter-cluster magnetic interaction plays an important role in the magnetic properties of the pseudo-binary intermetallic compounds $\text{La}(\text{Fe}_{1-x}\text{Al/Si}_x)_{13}$ as in the intra-cluster case.

In summary, high-resolution neutron diffraction was employed to investigate the crystallographic and magnetic structures in the NaZn_{13} -type intermetallic compound $\text{LaFe}_{11.4}\text{Si}_{1.6}$. In contrast to the Al preferential occupation of the 96i site in $\text{La}(\text{Fe}_{1-x}\text{Al}_x)_{13}$, Si atoms occupy both 8b and 96i sites randomly. The lattice parameter increases sharply with long-range ferromagnetic ordering and tightly correlates with the local Fe moments even in the low-temperature ferromagnetic state. The first-order magnetic phase transition is derived from this spontaneous magnetostriction jump and the coexistence of the large and small volume phases near the Curie temperature. The values of the spontaneous volume magnetostriction $\omega_s = 1.8\%$ at 2 K and the magnetovolume coupling constant $kC = 1.14 \times 10^{-8} \text{ cm}^6 \text{ emu}^{-2}$ are quite consistent with those in the FeNi–Invar alloys. After classifying the $\text{Fe}^{\text{II}}\text{--Fe}^{\text{II}}$ bond lengths into the inter-cluster and intra-cluster types, we find that the inter-cluster bond lengths are almost as short as the $\text{Fe}^{\text{I}}\text{--Fe}^{\text{II}}$ ones, and that the ferromagnetic state in $\text{La}(\text{Fe}_{1-x}\text{Si}_x)_{13}$ may prefer the longer Fe–Fe distances rather than the shorter ones. The inter-cluster magnetic interaction has the same importance as the intra-cluster ones to determine the magnetic properties of the pseudo-binary intermetallic compounds $\text{La}(\text{Fe}_{1-x}\text{Al/Si}_x)_{13}$.

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