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Magnetic transitions in LaFe13-x-yCoySix compounds

Jianli Wang
University of Wollongong, jianli@uow.edu.au

S J. Campbell
University of New South Wales, stewart.campbell@adfa.edu.au

S J. Kennedy
ANSTO

P Shamba
University of Wollongong, ps807@uowmail.edu.au

R Zeng
University of Wollongong, rzeng@uow.edu.au

See next page for additional authors

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Abstract

The magnetic properties of a set of LaFe13−x−yCoySix compounds (x = 1.6 – 2.6; y = 0, y = 1.0) have been investigated using magnetic measurements, thermal expansion, 57Fe Mössbauer spectroscopy and high resolution neutron powder diffraction methods over the temperature range 10–300 K. The natures of the magnetic transitions in these LaFe13−x−yCoySix compounds have been determined. The Curie temperatures of LaFe13−xSix were found to increase with Si content from TC = 219(5) K for Si content x = 1.6 to TC = 250(5) K for x = 2.6. Substitution of Co for Fe in LaFe10.4Si2.6 resulted in a further enhancement of the magnetic ordering temperature to TC = 281(5) K for the LaFe9.4CoSi2.6 compound. The nature of the magnetic transition at the Curie temperature changes from first order for LaFe11.4Si1.6 to second order for LaFe10.4Si2.6 and LaFe9.4CoSi2.6. The temperature dependences of the mean magnetic hyperfine field values lead to TC values in good agreement with analyses of the magnetic measurements. The magnetic entropy change, −ΔSM, has been determined from the magnetization curves as functions of temperature and magnetic field (ΔB = 0 – 5 T) by applying the standard Maxwell relation. In the case of LaFe12.4Si1.6 for example, the magnetic entropy change around TC is determined to be -ΔSM ~ 14.5 J kg−1 K−1 for a magnetic field change ∆ B = 0 − 5 T.

Authors

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Magnetic transitions in $LaFe_{13-x-y}Co_ySi_x$ compounds

J.L. Wang[1,2], S.J. Campbell[3], S.J. Kennedy[2], P. Shamba[1], R. Zeng[1], S.X. Dou[1] and G.H. Wu[4]

[1]Institute for Superconductivity and Electronic Materials, University of Wollongong, Wollongong, NSW 2522, Australia

[2]Bragg Institute, ANSTO, Lucas Heights, NSW 2234, Australia

[3]School of Physical, Environmental and Mathematical Sciences, The University of New South Wales Canberra, The Australian Defence Force Academy, ACT 2600, Australia

[4]National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, P.R. China

Abstract: The magnetic properties of a set of $LaFe_{13-x-y}Co_ySi_x$ compounds (x = 1.6-2.6; y = 0, y = 1.0) have been investigated using magnetic measurements, thermal expansion, ^{57}Fe Mössbauer spectroscopy and high resolution neutron powder diffraction methods over the temperature range 10 – 300 K. The natures of the magnetic transitions in these $LaFe_{13-x-y}Co_ySi_x$ compounds have been determined. The Curie temperatures of $LaFe_{13-x}Si_x$ were found to increase with Si content from T_C=219(5) K for Si content x=1.6 to T_C=250(5) K for x=2.6. Substitution of Co for Fe in $LaFe_{10.4}Si_{2.6}$ resulted in a further enhancement of the magnetic ordering temperature to T_C=281(5) K for the $LaFe_{9.4}CoSi_{2.6}$ compound. The nature of the magnetic transition at the Curie temperature changes from first order for $LaFe_{11.4}Si_{1.6}$ to second order for $LaFe_{10.4}Si_{2.6}$ and $LaFe_{9.4}CoSi_{2.6}$. The temperature dependences of the mean magnetic hyperfine field values lead to T_C values in good agreement with analyses of the magnetic measurements. The magnetic entropy change, $-\Delta S_M$, has been determined from the magnetization curves as functions of temperature and magnetic field (ΔB = 0-5 T) by applying the standard Maxwell relation. In the case of $LaFe_{12.4}Si_{1.6}$ for example, the magnetic entropy change around T_C is determined to be $-\Delta S_M \sim 14.5$ J kg^{-1} K^{-1} for a magnetic field change ΔB=0 -5 T.

1. Introduction

Magnetic refrigeration (MR) technologies based upon the magnetocaloric effect (MCE) offer scope for environmentally friendly cooling methods of higher cooling efficiency compared with conventional methods. Technologies based on MR [1, 2] have been considered as viable alternatives to several other solid-sate cooling methods [3] such as optical refrigeration [4], thermoelectric refrigeration [5] and electric refrigeration [6] . Since the incisive discoveries related to magnetic entropy changes at ferromagnetic transitions in the $Gd_5Si_{4-x}Ge_x$ series first reported by Pecharsky and Gschneidner in 1997 [7], materials with a large magnetocaloric effect have attracted significant attention with magnetic cooling applications in mind. Particular interest has focussed on the isothermal entropy changes at first-order magnetic transitions [3].

$LaFe_{13-x}Si_x$ compounds ($x \leq 1.6$) of the $NaZn_{13}$-type exhibit a large magnetic entropy change in the vicinity of Curie temperature T_C [8] and are typical of relatively low cost materials with potential as operational magnetic refrigerants around room temperature. The large entropy changes in $LaFe_{13-x}Si_x$ compounds are associated with the negative lattice expansion around T_C and the first-order field-induced paramagnetic (PM) to ferromagnetic (FM) itinerant electron metamagnetic transition above T_C [9]. Given that the Curie temperature of $LaFe_{13-x}Si_x$ is usually lower than 210 K, significant efforts have been made in order to enhance T_C and retain the larger MCE performance. Among the approaches taken are: (1) introduction of interstitial atoms (hydrogen or carbon) [10, 11]; (2) elemental substitution (substituting La [12, 13] and Fe [14, 15] by another rare-earth or transition metal), (3) modification of synthesis methods (arc-melting or induction-melting with various heat treatments [16], melt-spinning [17] and ball-milling [18]).

In this study, we report the findings of an investigation of the nature of the magnetic transitions in a set of $LaFe_{13-x-y}Co_ySi_x$ compounds ($x = 1.6$-2.6; $y = 0, 1.0$) by magnetic, [57]Fe Mössbauer spectroscopy, thermal expansion and neutron diffraction measurements. In agreement with previous studies [19, 20], the magnetic ordering temperature of $LaFe_{13-x}Si_x$ is found to increase steadily with Si content from T_C=219 K for x=1.6 to T_C=250 K for x=2.6. Pronounced enhancement to T_C=281 K is obtained on substitution of Co in the $LaFe_{9.4}CoSi_{2.6}$ compound.

2. Experimental

The $LaFe_{13-x-y}Co_ySi_x$ samples (x = 1.6, y = 0; x = 2.6, y = 0 and x = 2.6, y = 1.0) were prepared by standard arc melting and the ingots annealed in Ar atmosphere at 1000°C for 15 days, followed by quenching in water. The quality of the compounds was checked by both X-ray diffraction (XRD) analysis and thermomagnetic analysis (TMA). The magnetic properties of the compounds were measured in a superconducting quantum interference device (SQUID) and a Quantum Design Physical Property Measurement System (PPMS) over the temperature range 10 – 300 K for magnetic fields B = 0-5 T. Thermal expansion measurements were performed using a "push-rod" linear differential transformer method [21]. The Mössbauer spectra were obtained between 5 K and 300 K using a standard constant acceleration spectrometer and a $^{57}CoRh$ source. The spectrometer was calibrated at room temperature with an α-iron foil. Neutron diffraction experiments were carried out over the temperature range 10–300 K using the High-Resolution Powder Diffractometer Echidna (λ = 1.622 Å) at the OPAL reactor, Australia. The diffraction patterns were refined using the FULLPROF program package.

3. Results and Discussion

X-ray diffraction confirmed that all samples crystallize in the cubic $NaZn_{13}$-type structures with small amounts (~2% each) of the impurity phases (α-Fe and LaFeSi) being detected. The lattice parameters of the 1:13 phase are found to decrease from 11.468(5) Å to 11.443(5) Å as the Si content increases from x=1.6 to x=2.6 for $LaFe_{13-x}Si_x$. Substitution of Co atoms for the Fe atoms in the $LaFe_{10.4}Si_{2.6}$ compound leads to a further decrease in lattice parameter to 11.430(5) Å for $LaFe_{9.4}CoSi_{2.6}$. These results are very close to the values reported by Liu *et al.* [19].

For this structure there are two Fe sites: Fe_I - 8b site at (¼, ¼, ¼) and Fe_{II} - 96i site at (0, y, z) - and one La site 8a. Previous neutron studies [10] confirmed that the Si atoms are almost randomly distributed on the two Fe sites (8b and 96i), in contrast to the Al preferential occupation of the 96i site in $La(Fe_{1-x}Al_x)_{13}$. The reduction of the unit cell will directly influence the bonding distance between magnetic atoms. It is known that in Fe-based rare earth-transition metal compounds, the exchange interaction (and therefore the Curie

temperature) is mainly determined by the Fe–Fe exchange interaction which is sensitive to the Fe–Fe distance [19].

The temperature dependences of the ac susceptibility and dc magnetization for the three LaFe$_{13-x-y}$Co$_y$Si$_x$ samples (x = 1.6, y = 0; x = 2.6, y = 0 and x = 2.6, y = 1.0) are shown in Figures 1(a) and 1(b) for a measuring field of B =0.05 T. The magnetic ordering temperatures were determined from dχ/dT and dM/dT curves leading to the values T$_C$=219(5) K, T$_C$=250(5) K and T$_C$=281(5) K for LaFe$_{11.4}$Si$_{1.6}$, LaFe$_{10.4}$Si$_{2.6}$ and LaFe$_{9.4}$CoSi$_{2.6}$ respectively. The magnetization behaviours of LaFe$_{11.4}$Si$_{1.6}$, LaFe$_{10.4}$Si$_{2.6}$ and LaFe$_{9.4}$CoSi$_{2.6}$ were measured for fields in the range B =0-5 T around the regions of the magnetic ordering temperatures with analyses of these data leading to the related Arrott-plots of M^2 versus μ_0H/M as shown in Figures 2(a), (b) and (c), respectively.

The first order character of the LaFe$_{11.4}$Si$_{1.6}$ compound is indicated by the pronounced negative slopes and characteristic "S-bend" in the Arrott-plot of Figure 2(a). On the other hand the absence of either inflections or negative slopes in the Arrott plots of LaFe$_{10.4}$Si$_{2.6}$ and LaFe$_{9.4}$CoSi$_{2.6}$ indicates second-order magnetic transitions in these two compounds. These analyses of the Arrott plots for LaFe$_{13-x}$Si$_x$ (Figures 2(a), (b), (c)) demonstrate that the nature of the magnetic transitions transforms with increasing Si content from first order (T$_C$=219(5) K; x=1.6) to second order (T$_C$=250(5) K; x=2.6) in full agreement with previous studies ([19]; see [20] for a review of LaFe$_{13-x}$Si$_x$-based alloys). The increasing Si content in LaFe$_{13-x}$Si$_x$ compounds causes two main effects: (1) lattice contraction and (2) hybridization between the electronic orbital of Si and Fe (the cause of the reduction in the Fe magnetic moment). Even though both the La–Fe inter-atomic distances and the lattice constants decrease with increasing Si content, the average Fe–Fe distance increases; this behaviour may be responsible for the increase of T$_C$ [19]. The substitution of Co for Fe leads to a further enhancement in the Curie temperature for LaFe$_{9.4}$CoSi$_{2.6}$ up to T$_C$=281(5) K compared with T$_C$=250(5) K for the Co-free compound LaFe$_{10.4}$Si$_{2.6}$.

According to the conventional static scaling law (see e.g. [21, 22] and references therein), the critical properties of a second-order magnetic transition can be described by the critical exponents β, γ and δ as derived from magnetization measurements around the transition temperature. The Kouvel-Fisher method offers an accurate and relatively straightforward way of determining the critical exponents [23]. We have applied the Kouvel-Fisher method and

related analyses (see [24] for a full outline of the analytical procedures) to derive the values of β = 0.52, γ = 0.76 and δ=2.46 for LaFe$_{10.4}$Si$_{2.6}$. The mean field interaction model for long range ordering has theoretical critical exponents of β = 0.5, γ = 1.0 and δ = 3.0, while theoretical values based on the three dimensional Heisenberg model corresponding to short range interactions are β = 0.365, γ = 1.386 and δ = 4.80 [e.g. 25]. The values we have derived for β, γ and δ for LaFe$_{10.4}$Si$_{2.6}$ are generally similar to the mean-field model values.

The magnetic entropy values, -ΔS_M, for LaFe$_{11.4}$Si$_{1.6}$ around the first order ferromagnetic ordering temperature for fields up to B = 5 T are shown in Fig. 2(d). The changes in magnetic entropy were derived from the magnetisation measurements using the standard Maxwell relationship as applied, for example, in the case of NdMn$_2$Ge$_{0.4}$Si$_{1.6}$ [26]. The maximum value of -ΔS_M ~ 14.5 J kg^{-1} K^{-1} was obtained centred around ~ 195 K with a half-width spread of ΔT ~ 20 K for a magnetic field change ΔB = 0-5 T. This corresponds to a refrigerant capacity, RC, (product of the maximum value of -ΔS_M and the full width at half maximum of the -ΔS_M curve) of RC ~ 290 J kg^{-1} for field changes ΔB = 0–5 T, which is lower than the values reported previously for both bulk (RC ~ 467 J/kg) [27] and ball milled (RC ~ 439 J/kg) [28] samples of LaFe$_{11.4}$Si$_{1.6}$. This may be due to variations in the sample compositions.

Thermal expansion measurements have been obtained around the Curie temperatures for the LaFe$_{11.4}$Si$_{1.6}$, LaFe$_{10.4}$Si$_{2.6}$ and LaFe$_{9.4}$CoSi$_{2.6}$ samples along with a further LaFe$_{11}$Si$_2$ sample using the push-rod method [29, 30]. The temperature dependences of the linear thermal expansions (LTE) are shown in Figure 3 with pronounced magneto-volume effects detected around T$_C$ for all compounds (the LTE coefficient for LaFe$_{11.4}$Si$_{1.6}$ is shown as an inset). In agreement with the first order character of the magnetic transition of LaFe$_{11.4}$Si$_{1.6}$, the LTE changes are found to be sharper than those observed for the second order transitions of LaFe$_{10.4}$Si$_{2.6}$ and LaFe$_{9.4}$CoSi$_{2.6}$. The dashed lines in Figure 3 represent the contributions to the total expansion due to the linear lattice thermal expansion ($\Delta l/l$)$_{lat}$. Subtraction of the phonon contribution to the thermal expansion enables the net effect due to the spontaneous magnetostriction to be estimated. This lattice contribution has been extrapolated from the paramagnetic regime where only the phonon anharmonic contribution is expected. The extrapolation was performed using the Grüneisen-Debye model, with a Debye temperature θ_D = 300 K [31] (differences in the values of θ_D do not in practice affect the physical analysis of the magneto-volume origin, but only lead to a shift in the value of the spontaneous

magnetostriction, which is outside the scope of our interest here). It is well known that the magnetovolume effect in R-Fe based compounds is related to the weak ferromagnetic character of 3d magnetic moments. It is interesting to note that, for the $LaFe_{10.4}Si_{2.6}$ compound, the thermal expansion is very close to zero below ~155 K (see Figure 3). This is demonstrated by the extrapolation of the thermal expansion data towards absolute zero (dotted horizontal line in Figure 3) and indicates the potential of this sample for zero thermal expansion materials applications.

The magnetostructural behaviour of the $LaFe_{11.4}Si_{1.6}$ compound has been investigated further by variable temperature powder neutron diffraction measurements (λ = 1.622 Å) over the temperature range 10–300 K in applied magnetic fields B=0 T, 1 T, 6 T. Examples of the neutron diffraction patterns for $LaFe_{11.4}Si_{1.6}$ are shown in Figure 4(a) with the refinement of the 10 K pattern shown as an example. As shown by the variation of the a_0 lattice parameter with temperature in Figure 4(b), the refinement results confirm that for ambient conditions below T_C in zero magnetic field, the unit cell experiences a large expansion of $\Delta a_0/a_0$ ~ 0.27%, corresponding to ~ 0.81% increase in the unit cell volume. It is well accepted that the magneto-volume effect is caused by the expansion resulting from the spontaneous magnetostriction which cancels the normal thermal contraction. While data for applied fields of B = 1 T and B = 6 T were only available to 250 K compared with up to 300 K for B = 0 T, it is evident from the shift in the lattice parameter values to 250 K of Figure 4(b), that the applied magnetic field shifts the T_C values of the Curie temperature to higher temperatures.

The Mössbauer spectra for $LaFe_{9.4}CoSi_{2.6}$ in Figure 5(a) are shown as representative examples for the set of $LaFe_{13-x-y}Co_ySi_x$ compounds. Similar to references [15, 19], the magnetic spectra were fitted using a distribution model of hyperfine fields with the paramagnetic spectra being fitted with doublets. The resultant fits are shown by the dashed lines through the data of Figure 5(a) with the field distributions providing values of, $<B_{hf}>$, the mean magnetic hyperfine field for all samples. The local magnetic behaviours of the Fe atoms of the $LaFe_{13-x-y}Co_ySi_x$ compounds is reflected by the graphs of $<B_{hf}>$ versus temperature for the $LaFe_{11.4}Si_{1.6}$, $LaFe_{10.4}Si_{2.6}$ and $LaFe_{9.4}CoSi_{2.6}$ samples as shown in Figure 5(b). Consistent with the outcomes from the Arrott plot analyses of the magnetisation data, the $LaFe_{11.4}Si_{1.6}$ sample is found to exhibit a relatively sharp decrease in hyperfine field at the first order transition T_C=219(5) K compared with the rate of change of hyperfine field with temperature

for the second order transitions at T_C=250(5) K and T_C=281(5) K of the $LaFe_{10.4}Si_{2.6}$ and $LaFe_{9.4}CoSi_{2.6}$ samples respectively, in good agreement with previous studies [15].

4. Conclusions

Analyses of the magnetisation data of a set of $LaFe_{13-x-y}Co_ySi_x$ compounds (x = 1.6, y = 0; x = 2.6, y = 0 and x = 2.6, y = 1.0) have confirmed that the natures of the magnetic transitions change from first order for $LaFe_{11.4}Si_{1.6}$ to second order for $LaFe_{10.4}Si_{2.6}$ and $LaFe_{9.4}CoSi_{2.6}$. The behaviour of these samples as investigated by thermal expansion and Mössbauer spectroscopy agrees well with the bulk magnetic properties. Pronounced positive spontaneous volume magnetostriction has been observed below T_C which can be attributed to volume dependence of the magnetic energy. The $LaFe_{13-x-y}Co_ySi_x$ compounds are shown to exhibit pronounced values of negative thermal expansion around the Curie temperatures in good agreement with recent reports of giant negative thermal expansion in $La(Fe,Si)_{13}$-based compounds with the $NaZn_{13}$-type structure [32]. In addition the $LaFe_{10.4}Si_{2.6}$ compound is found to exhibit close to zero thermal expansion below ~155 K.

Acknowledgments

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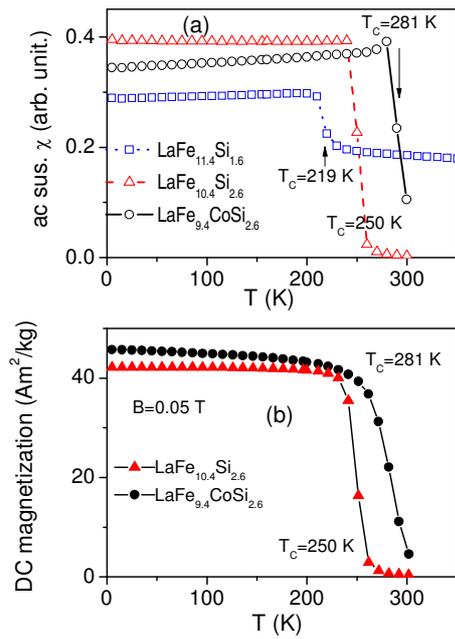
Figure 1 Temperature dependence of the (a) ac susceptibility and (b) DC magnetization for the set of $LaFe_{13-x-y}Co_ySi_x$ samples (x = 1.6, y = 0; x = 2.6, y = 0; and x = 2.6, y = 1.0). Measurements were made in a field of B = 0.05 T; the dashed and full lines act as guides to the eye.
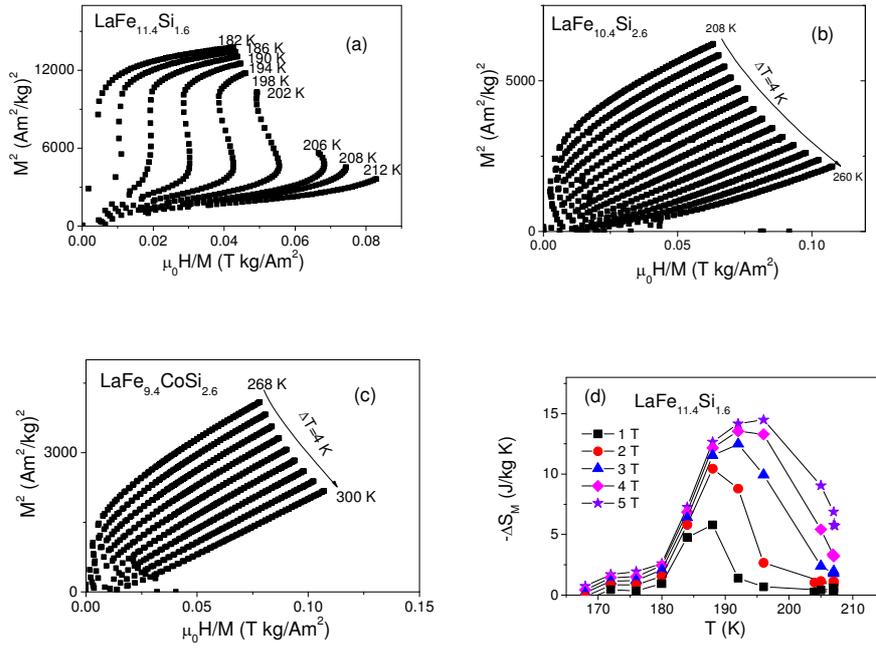
Figure 2 Arrott plot analyses (M^2 versus μ_0H/M curves) around the magnetic transition region for (a) LaFe$_{11.4}$Si$_{1.6}$, (b) LaFe$_{10.4}$Si$_{2.6}$ and (c) LaFe$_{10.4}$CoSi$_{2.6}$.

(d) The magnetic entropy changes, -ΔS_M, for LaFe$_{11.4}$Si$_{1.6}$ around the first order ferromagnetic ordering temperature. The magnetic entropy values were calculated using decreasing fields.

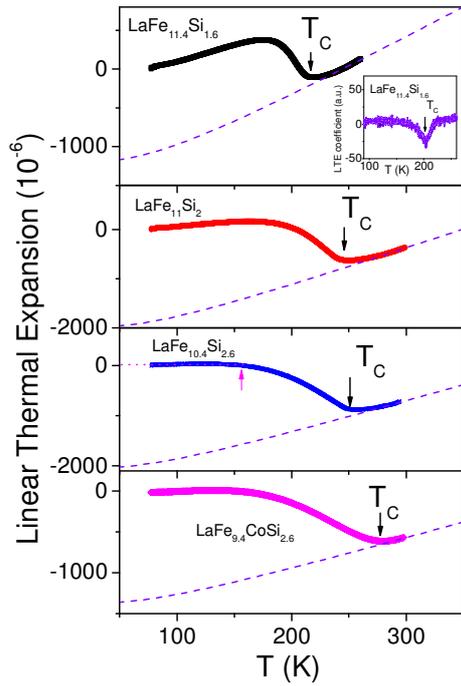Figure 3 The variation of the linear thermal expansion of $LaFe_{11.4}Si_{1.6}$, $LaFe_{11}Si_2$, $LaFe_{10.4}Si_{2.6}$ and $LaFe_{9.4}CoSi_{2.6}$ samples in the region of their Curie temperatures. The LTE coefficient for $LaFe_{11.4}Si_{1.6}$ is shown in the inset. As discussed in the text, the dashed lines represent the phonon contribution to the thermal expansion. Also as discussed, the thermal expansion is close to zero for $LaFe_{10.4}Si_{2.6}$ below ~155 K (indicated by the arrow).
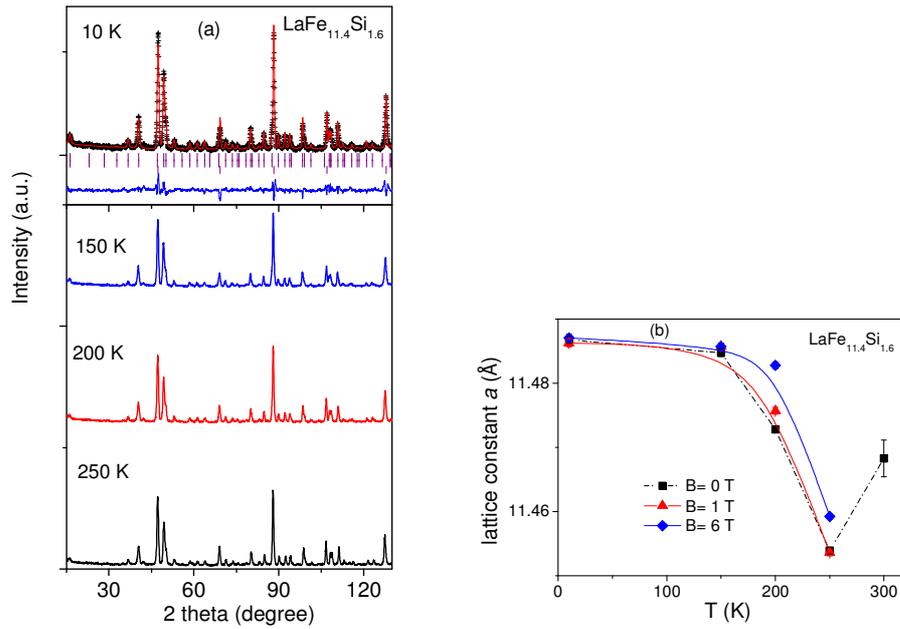
Figure 4 (a) Neutron diffraction patterns (λ = 1.622 Å) of the LaFe$_{11.4}$Si$_{1.6}$ sample at the temperatures indicated. The Rietveld refinement of the 10 K pattern is shown as an example. (b) A graph of the lattice parameters for LaFe$_{11.4}$Si$_{1.6}$ as a function of temperature as determined for the set of neutron diffraction patterns measured in applied magnetic fields (B = 0 T, 1 T, 6 T). The full and dashed lines act as guides to the eye.
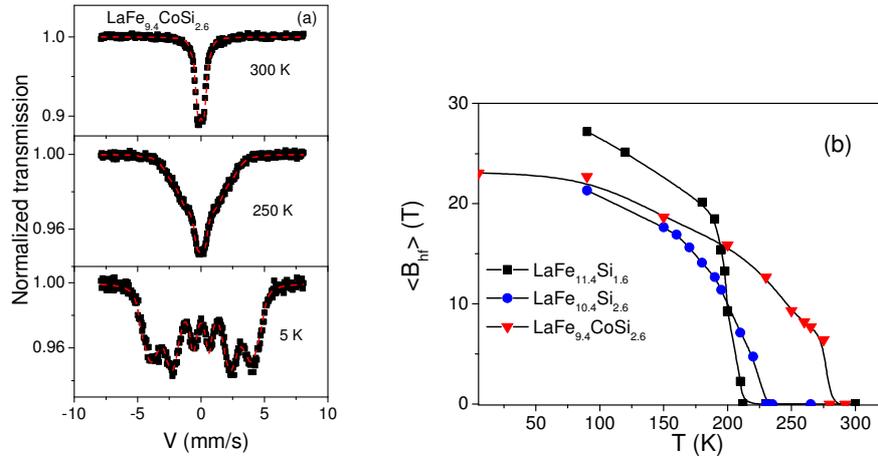
Figure 5(a) Mössbauer spectra of the LaFe$_{9.4}$CoSi$_{2.6}$ sample at room temperature, 259 K and 5 K. The dashed lines represent fits to the spectra as described in the text.

(b) The temperature dependence of, <B$_{hf}$>, the mean magnetic hyperfine field values for the LaFe$_{11.4}$Si$_{1.6}$, LaFe$_{10.4}$Si$_{2.6}$ and LaFe$_{9.4}$CoSi$_{2.6}$ samples as determined from the fits to the spectra. The full lines act as guides to the eye.