Magnetovolume effect in intermetallics LaFe$_{13-x}$Si$_x$

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Abstract
Based on the Bean–Rodbell model, which assumes a linear variation
of exchange coupling with atom spacing, the magnetovolume effects in
$LaFe_{13-x}Si_x$ ($x = 1.2$–2.0) have been systematically studied. A relation
between phase volume and magnetization is first obtained by comparing the
structural and magnetic data collected at various temperatures. The maximum
spontaneous magnetostriction thus derived is dependent on the content of Si,
linearly decreasing from $\sim$2.15% for $x = 1.2$ to $\sim$1.12% for $x = 2$. Based
on these results and limited experimental data, the parameters involved in the
Bean–Rodbell model are determined for the $LaFe_{13-x}Si_x$ compounds. Further
analysis indicates that the Bean–Rodbell model equipped with these parameters
gives a satisfactory description of the magnetovolume effects produced by
interstitial hydrogen for the $LaFe_{11.44}Si_{1.56}$ hydride. To explain the pressure
effects, in contrast, changes of the parameters under pressure, which are a result
of the enhancement of the first-order character of the phase transition, have to be
taken into account. These results indicate that either the increase or the decrease
of the Curie temperature is simply a consequence of the variation of the phase
volume due to the introduction of interstitial atoms or the application of a high
pressure, and can be described well by the Bean–Rodbell model.

1. Introduction

A giant magnetocaloric effect has recently been observed in the intermetallics $LaFe_{13-x}Si_x$
(LFS) [1, 2]. It occurs accompanying a first-order magnetic transition, which causes a sharp
magnetization drop, and thus a great entropy increase. The entropy change can be as high as
$\sim$20 J kg^{-1} K^{-1}, nearly double that of Gd ($\sim$12 J kg^{-1} K^{-1}), for a magnetic field change of
0–5 T even near the ambient temperature.

In contrast to MnAs and $Gd_5Si_{4-x}Ge_x$, LFS exhibits an isotropic lattice expansion, without
structure changes, at the magnetic transition, and the relative volume change can be as large as

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1.3% [2–4]. Signatures of strong magnetoelastic coupling are also observed in this compound. It was found that the magnetic transition shifts to high temperatures when the lattice expands due to, for example, the introduction of interstitial hydrogen, and a lattice expansion of ∼2.1% can lead to an increase of the Curie temperature by ∼140 K [5]. In contrast to Si doping, which drives the magnetic transition from first order to second order, in the meantime increasing the Curie temperature, the magnetic transition maintains a first-order nature as the Curie temperature increases. However, when the lattice shrinks under high pressure or on replacing La with smaller rare-earth atoms, the transition temperature decreases. It has been revealed that a pressure of 1 GPa can reduce the Curie temperature by ∼90 K [6, 7]. Although the introduction of interstitial hydrogen and the application of a high pressure produce different effects, a common feature of the two processes is the variation of the phase volume of the compound, either expansion or contraction. These results indicate the presence of a close relation between the ferromagnetic (FM) coupling and the atom spacing in LFS: the former enhances/weakens as the atom spacing increases/decreases.

These results actually imply a simultaneous variation of exchange and elastic energies, and thus magnetic and lattice entropies, which is a hot topic of recent researches. There is evidence that the contributions to the magnetocaloric effects from the latter and the former are comparable [8, 9]. Therefore, a systematic study of the magnetoelastic coupling is obviously important for the understanding and controlling of the entropy changes in LFS and related materials.

In fact, for a compound that experiences a first-order phase transition, the transition temperature (T_a) is not the measure of the exchange coupling in either the FM or the paramagnetic (PM) phase. It will take a value in between the Curie temperatures of these two phases. Bean and Rodbell have proposed a simple relation $T_C = T_0(1 + \beta\omega)$ to describe the magnetoelastic coupling in this case [10], where T_C and T_0 are the Curie temperatures of the FM and the PM phases, respectively, and $\omega = (V - V_0)/V_0$ (V_0 is the volume without exchange interactions) is the relative volume change. This formula suggests a linear increase of the Curie temperature of the FM phase with the growth of the atom spacing. Based on it, the magnetovolume effects in MnAs can be qualitatively explained.

In this paper, we will first examine the applicability of the Bean–Rodbell model to LFS, then attempt to determine the parameters involved in this model for the LFS system based on limited experiment data and, furthermore, provide a quantitative analysis for the magnetovolume effects in LFS. It is found that either the increase or the decrease of the Curie temperature could be simply a consequence of the variation of the phase volume due to, for example, the introduction of interstitial atoms or the application of a high pressure, and can be described well by the Bean–Rodbell model.

2. Experiment

LaFe$_{13-x}$Si$_x$ (LFS) samples with $x = 1.2$, 1.4, 1.6, 1.8, and 2 were prepared by arc melting appropriate amounts of starting materials (99.9% in purity) under ultrapure argon atmosphere (∼10 at.% excessive La was used to compensate for the weight loss during the arc melting). The resultant ingots were first annealed in an evacuated quartz tube for one month at 1050 °C to improve the crystallization of the sample and then quenched into liquid nitrogen.

The phase purity and crystal structure of the resultant samples are studied with a MAC Science x-ray diffractometer (M18-AHF) equipped with a cryostat (20–300 K), and the magnetic properties were measured by a superconducting quantum interference device (SQUID) magnetometer. All the data presented here was collected during the warming process after zero-field cooling the sample to the predetermined temperatures.
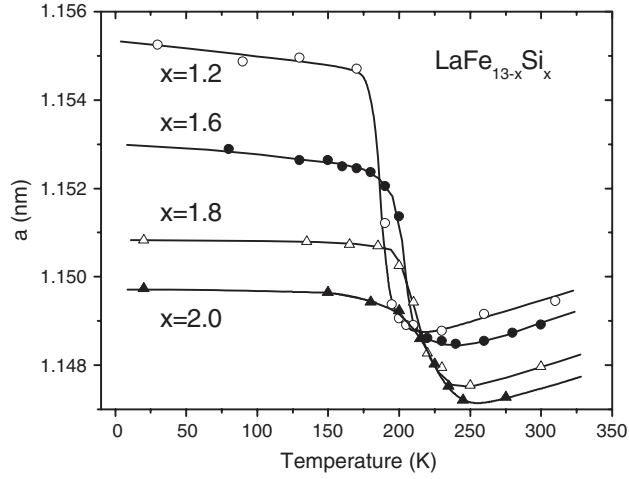
Figure 1. Lattice constant as a function of temperature for selected LFS samples. The solid lines are guides for the eye.

3. Spontaneous magnetostriction

The x-ray diffraction (XRD) study indicated that the samples are of single phase with a cubic structure for $x \geqslant 1.4$ and that they contain minor α-Fe for $x < 1.4$ ($\sim$2–6% in weight fraction according to the analyses of the Rietveld refinement of the XRD spectra and magnetic measurements). Figure 1 shows the lattice constants, deduced from the XRD data, as functions of temperature for different compositions. The most remarkable observations are the gradual decrease of lattice constant with the increase of temperature in the low-temperature range, instead of thermal expansion, and the sharp lattice contraction at a definite temperature of x-dependence, which is also the temperature of the magnetic transition. The former can be ascribed to thermal spin fluctuation, which leads to a reduction of magnetization, and thus a lattice shrinkage, as will be seen below, and the latter reveals the very different phase volume of the FM and the PM phases. These results are in qualitative agreement with those reported previously by different authors.

Based on the Bean–Rodbell relation, the Gibbs free energy per volume is, within the mean field approximation [11],

$$G(T, P, H) = -\frac{3J}{2(J+1)} N k_B T_0 (1 + \beta\omega)\sigma^2 + \frac{1}{2} B\omega^2 - TS + P\omega - HgJ\mu_B N\sigma, \qquad (1)$$

where k_B is the Boltzmann constant, N the number of spins per volume, J the quantum number of spins, $\sigma = M/(NgJ\mu_B)$ the normalized magnetization, B the bulk elastic modulus of LFS, P the pressure, g the Landè g-factor, and H the magnetic field. The first term describes the exchange energy, the second term the elastic energy, and the last term the Zeeman energy. With the use of the equality $\partial G/\partial\omega = 0$, a requirement for thermal equilibrium, it is easy to obtain that

$$\omega = \frac{3J}{2(J+1)B} N k_B T_0 \beta\sigma^2 - P/B. \qquad (2)$$

Under the ambient pressure, the second term is unimportant compared with the first one, and can be omitted. This equation relates the phase volume to the magnetization. The prefactor $3J N k_B T_0 \beta/[2(J+1)B]$ of the first term is the maximum spontaneous magnetostriction: the

volume change when the system transforms from a fully magnetically ordered state into a completely disordered state. It varies proportionally to T_0, β and the reciprocal of B. This relation can be experimentally examined since both ω and σ are measurable quantities.

It is obvious that spontaneous magnetization should be used to compare with the lattice constant to avoid the modification of external field to magnetic behaviours. Unfortunately, it is difficult to obtain an exact spontaneous magnetization for LFS, especially near the transition point, by simply extrapolating high-field data to $H \rightarrow 0$ because of the occurrence of the field-induced metamagnetic transition. After careful consideration, we collected the magnetization data under a field of 1 T, which can effectively eliminate undesired extrinsic effects without significantly affecting the magnetic transition. The magnetization as a function of applied field, recorded at different temperatures in the vicinity of T_a, is shown in figure 2(a) for the sample with $x = 1.6$. The square of the normalized thermal magnetization curves is shown in figure 2(b). It is obvious that the abnormal lattice variation below T_C is a combined effect of the thermal expansion and the spontaneous magnetostriction. To compare the lattice variation and the magnetization, the thermal expansion should be corrected, which is not an effect of magnetic origin. This implies that $(\Delta a/a - \gamma T) = JNk_B T_0 \beta \sigma^2/[2(J + 1)B]$ if a linear thermal expansivity (γ) independent of temperature is assumed. The parameters involved in this equation can be determined by fitting the $a(T)$ relation (lattice constant) to the $\sigma(T)^2$ relation. A field of 1 T may cause a high temperature shift of T_a by $\sim$4 K. This factor is considered during the curve-fitting by simply shifting the ω–T curve upwards. The lattice constants, after a thermal expansion correction and an appropriate amplification, are also presented in figure 2(b) for comparison. After optimizing the fitting parameters, a satisfactory agreement between the two sets of data is observed in the whole temperature range from 20 to 300 K, especially near the Curie temperature, where rapid changes in a and σ take place.

Based on the above analyses, the thermal expansion and the spontaneous magnetostriction of LFS can be derived. The linear thermal expansivity is $\sim$8.2 $\times$ 10^{-6} K^{-1}, essentially independent of the Si content of the compound. This value is similar to that observed in ordinary metals and intermetallics. Meanwhile, the parameter $3JNk_B T_0 \beta/[2(J + 1)B]$ takes a value between $\sim$0.0215 and $\sim$0.0112, depending on the content of Si (figure 3). It decreases approximately linearly with the increase of x, and nearly halves on going from $x = 1.2$ to 2.0. Although it is small, a simple analysis reveals that considerable magnetostriction exists until $x \approx 2.85$. The nature of the magnetic transition can be analysed based on Landau theory [10]. The transition is of first order if $\eta = 40J^2(J+1)^2 Nk_B T_0 \beta^2/[(2J+1)^4 - 1]B > 1$, while it is of second order when $\eta < 1$. η changes from above 1 to below 1 with the increase of x, as will be seen in the next section. Therefore, the decrease of the spontaneous magnetostriction reflects the weakening of magnetoelastic coupling, and thus the evolution of the magnetic transition from first order to second order. One thing deserving special attention is that although there is considerable magnetostriction, the magnetic transition can be of second order. The meaning of this result is twofold. The first one is that the volume change is not an exclusive criterion for the first-order phase transition. The second one is that the σ–T dependence can be different even for a second-order phase transition, varying with η.

In fact, the $\omega \propto \sigma^2$ relation has been previously verified in the temperature range below T_a for a special sample $x = 1.6$, and the maximum spontaneous magnetostriction obtained is $\sim$0.018, a value similar to that derived here [12].

4. Determination of the model parameters

According to equation (2), the spontaneous magnetostriction is determined by T_0 and β, which can be extracted from the limited experimental data of LFS. According to the Bean–Rodbell
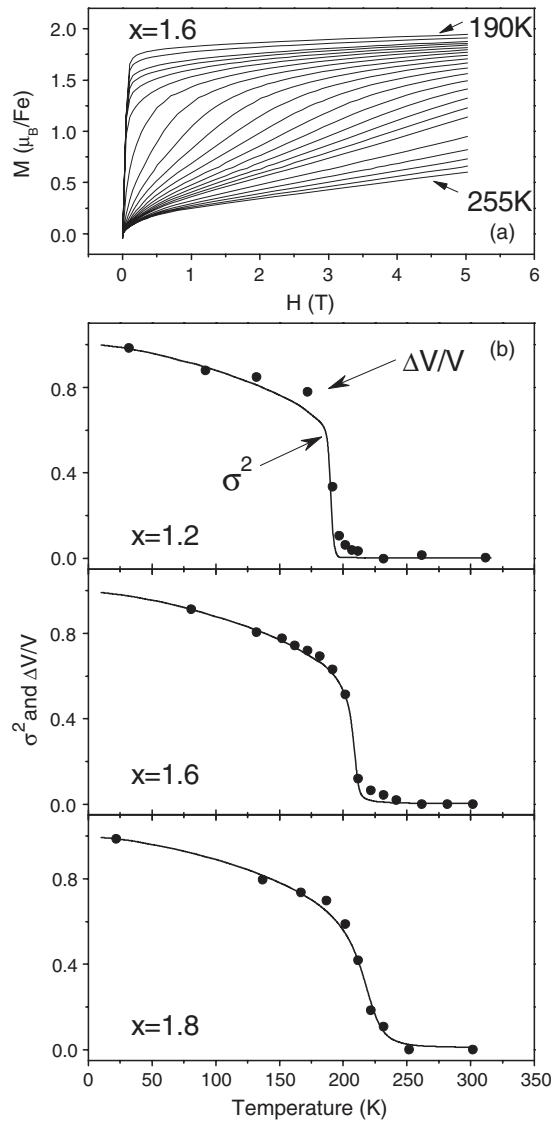
Figure 2. (a) Magnetization as a function of applied field for the sample with $x = 1.6$, recorded at different temperatures. The temperature step is 2 K in the vicinity of the T_a, from 200 to 230 K, and 5 K in the regions of 190–200 K and 230–255 K. (b) Temperature dependence of the square of the normalized magnetization (σ^2) and the relative volume change ($\Delta V/V$) after thermal expansion correction and proper amplification.

relation, the first-order transition takes place at a temperature $T_a \geqslant T_0$. The latter is the Curie temperature of the PM phase, and it can be determined by the Curie–Weiss law based on thermal magnetization data. Figure 4 shows T_0 and T_a as functions of x, and the inset plot is a demonstration for the derivation of T_0. It is clear that T_0 is significantly smaller than T_a when x is small, approaches T_a as x increases, and reaches T_a at $x = 1.8$. It is interesting to note that when $x \geqslant 1.8$ the magnetic phase transition in LFS changes from first order to second order; thus $T_a \approx T_0$.
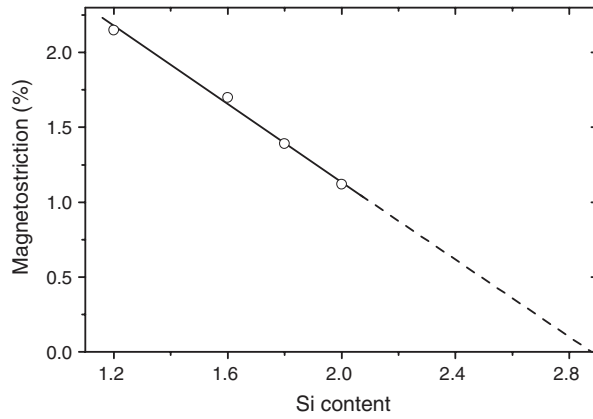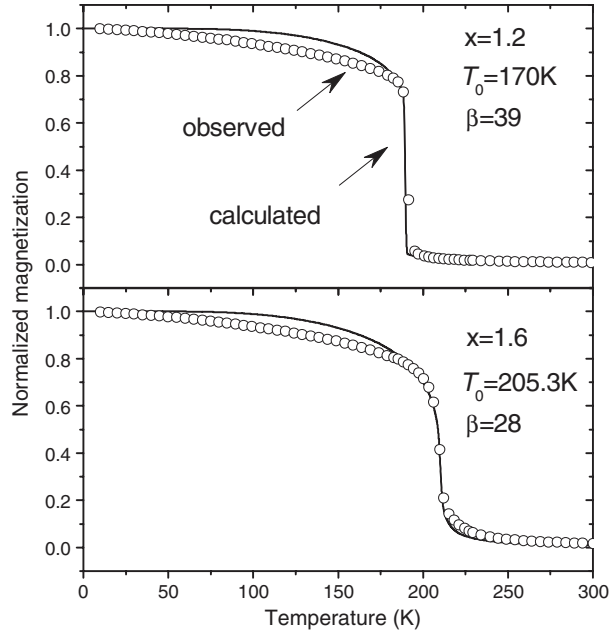
Figure 3. The maximum spontaneous magnetostriction as a function of Si content in LFS. The solid and dashed lines are guides for the eye.
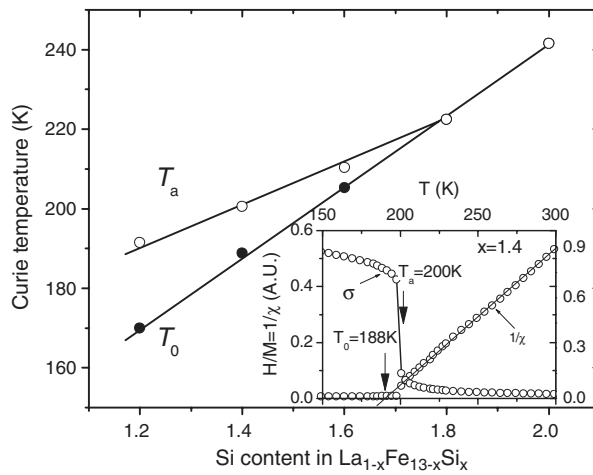
Figure 4. Paramagnetic Curie temperature (T_0) and the transition temperature (T_a) as functions of Si content in LFS. The inset plot shows the reduced thermal magnetization curve and the Curie–Weiss fitting of the magnetic data for the LFS sample with $x = 1.4$ ($H = 1$ T). The solid lines in the figure and the inset are guides for the eye.

β is a key parameter characterizing the structure sensitivity of magnetic interaction in the Bean–Rodbell relation. Based on the mean-field theory, we can calculate the temperature dependence of magnetization $\sigma = B[(H_{\text{eff}} + H)gJ\mu_B/k_BT]$ utilizing the molecular field $H_{\text{eff}} = \lambda NgJ\mu_B\sigma$, where $B(x)$ is the Brillouin function, $\lambda = 3k_BT_C/[Ng^2\mu_B^2J(J+1)]$, and $T_C = T_0(1 + \beta\omega)$. $J = 1.1$ (deduced from saturation magnetization recorded at 5 K under a field of 5 T) and $g = 2$ are adopted in the calculation. The only adjustable parameter is β, which is set to the value that properly restores the σ–T relation, particularly the transition temperature T_a. The equation $\sigma = B[(H_{\text{eff}} + H)gJ\mu_B/k_BT]$ can be self-consistently solved. Figure 5 is a comparison of the calculated and measured σ–T relations for selected samples with $x = 1.2$ and 1.8. The β value thus obtained varies between 16.5 and 39, as a function of x. The corresponding bulk elastic modulus is 1.98–2.29 × 10^7 N cm^{-2}, similar to that of Fe

Figure 5. Measured and calculated thermal magnetization curves with the parameters indicated for selected samples with $x = 1.2$ and 1.6.

Table 1. Parameters involved in the Bean–Rodbell model and the corresponding maximum spontaneous magnetostriction.

x	T_a	T_0	β	B (10^7 N cm^{-2})	$3JNk_BT_0\beta/[2(J+1)B]$	η
1.2	191.5	170.0	39.0	1.98	0.0215	2.34
1.6	210.3	205.3	28.0	2.18	0.0170	1.27
1.8	222.4	222.4	22.0	2.26	0.0139	0.82
2.0	241.5	241.5	16.5	2.29	0.0112	0.49

($\sim 1.68 \times 10^7$ N cm^{-2}) [13]. Table 1 gives the parameters involved in the Bean–Rodbell model and the corresponding maximum spontaneous magnetostriction.

Considerable uncertainty occurs for the determination of β in the case of $x = 1.6$–2.0 because of the broadening of the magnetic transition, which could be a combined effect of intrinsic broadening and sample inhomogeneity. As a supplement, we would like to point out that the presence of a small amount of α-Fe does not influence our conclusion. The magnetization of α-Fe is nearly constant in the temperature range concerned because of the high Curie temperature of Fe (~ 1043 K), and has been subtracted from the total magnetization in our calculation.

With the known T_0, β, and B, η can be calculated, which is a parameter for the characterization of the phase transition. It varies from ~ 2.34 to ~ 0.49 as the Si content of LFS increases from 1.2 to 2.0. Compared with LFS, the first-order character of the phase transition in MnFeP$_{0.45}$As$_{0.55}$ ($\eta = 1.4$) is much weaker than that of LFS ($x = 1.2$), and comparable to that of LFS ($x = 1.6$). It is interesting to note that the entropy change of MnFeP$_{0.45}$As$_{0.55}$ is also between those of samples of LFS with $x = 1.2$ and 1.6. However, the PM Curie temperature of the LFS family is lower than that of MnFeP$_{0.45}$As$_{0.55}$ ($T_0 = 296$ K). This explains the low T_a of LFS.

5. Discussion

As has been experimentally proved, for the LFS compound the magnetic transition shifts to high or low temperatures when the lattice expands or shrinks. These results indicate the presence of a close relation between the FM coupling and the atom spacing. It would be interesting to check whether the Bean–Rodbell relation equipped with the parameters listed in table 1 really gives a proper description for the magnetoelastic coupling in LFS. A typical magnetovolume effect is the enhancement of the magnetic coupling in LFS after introducing interstitial hydrogen. It has been reported that the transition temperature of the sample with the nominal composition $LaFe_{11.44}Si_{1.56}H_\delta$ increases from $T_a \sim 195$ K to ~ 336 K if the hydrogen content, which here has a value of $\delta = 1.6$, is absorbed. An XRD study revealed a volume expansion of $\sim 2.1\%$ due to the presence of interstitial hydrogen [5]. It is obvious that the lattice expansion could affect the Curie temperature of either the low- or the high-temperature phase. Take the high-temperature phase as an example. A simple calculation indicates that the lattice expansion will lead to a new T_0. Noting the fact that the transition temperature (T_a) of $LaFe_{11.44}Si_{1.56}$ (~ 195 K) is in between those of our $x = 1.2$ ($T_a = 191.5$ K) and $x = 1.6$ ($T_a = 210.3$ K) samples, a direct extrapolation gives $T_0 \approx 176$ K and $\beta \approx 37$. Therefore, the new T_0 after the interstitial hydrogen is loaded will be $T_0 = 176 \times (1 + 37 \times 0.021) \approx 313$ K ($\omega = 2.1\%$). If the presence of interstitial atoms does not influence the first-order character of the magnetic transition for LFS, which is a plausible assumption according to the work of Fujita *et al* [14], the difference between T_a and T_0 (~ 20 K) will be approximately retained. This actually implies that the new T_a will be ~ 333 K. It is a value in satisfactory agreement with the observed one, ~ 336 K. It is easy to see that the effects of interstitial hydrogen would be weakened when the content of Si is high, due to the decrease of η and β. This is also the apparent reason for the evolution of the magnetic transition from first order to second order.

In contrast, the magnetic transition will be depressed when a high pressure is applied. Fujita *et al* found a reduction of ~ 90 K in the transition temperature of $LaFe_{11.44}Si_{1.56}$ under a pressure of 1 GPa [6, 7]. In contrast to the situation with interstitial hydrogen, high pressure could produce a volume contraction of the compound. It is easy to calculate that the relative volume change will be $P/B \approx 0.5\%$ under a pressure of 1 GPa if $B \approx 2 \times 10^7$ N cm^{-2} is adopted for $LaFe_{11.44}Si_{1.56}$. As with the situation with interstitial hydrogen, a new T_0 for the system under the pressure of 1 GPa could be calculated with the expression $T_0 = 176 \times (1-37 \times 0.005) \approx 143$ K. Considering the relation $T_a > T_0$, T_a evaluated in this way will be much larger than the experimentally observed $T_a = 105$ K. The reason for this discrepancy may be that the parameters used here were derived under ambient pressure. It is obvious that to describe the system under high pressures, parameters under the corresponding conditions should be used. This is different from the case of hydrogen doping. As proved by Fujita *et al* [14], the thermomagnetization curves of $LaFe_{11.44}Si_{1.56}H_\delta$ shift nearly rigidly to high temperatures with increasing hydrogen content, which actually implies the maintenance of the character of the phase transition though the change of the Curie temperature is as large as ~ 140 K.

As for the pressure effect, it can be seen from [7] that accompanying the decrease of the Curie temperature (T_a) with pressure, the magnetic transition becomes increasingly sharp. This suggests an enhancement of the first-order character of the phase transition, and thus a variation of T_0 and β. This has been confirmed by an analysis of the magnetization isotherm obtained under a pressure of 0.8 GPa for the compound $LaFe_{11.5}Si_{1.5}$, the only data available for us (not shown). If B remains as 2×10^7 N cm^{-2}, we obtained that $T_0 \approx 47$ K and $\beta \approx 183$ for this compound. The new T_0 and β can be checked by the expression $T_0 = 176 \times (1-183 \times 0.004) \approx 47$ K ($P/B \sim 0.4\%$). These results indicate that this gives a satisfactory description of the pressure effect as well.

6. Summary

Based on the Bean–Rodbell model, which assumes a linear variation of the exchange coupling with atom spacing, the magnetovolume effects in LaFe$_{13-x}$Si$_x$ ($x = 1.2$–2.0) have been studied systematically. A relation between phase volume and magnetization is first obtained by comparing the structural and magnetic data collected at various temperatures. The maximum spontaneous magnetostriction thus derived is found to be strongly Si content dependent, linearly decreasing from ∼2.15% for $x = 1.2$ to ∼1.12% for $x = 2$. Based on these results and the magnetic data, the parameters involved in the Bean–Rodbell model are determined. Further analysis indicates that the Bean–Rodbell model equipped with these parameters gives a satisfactory explanation for the magnetovolume effects produced by the introduction of interstitial hydrogen for the LaFe$_{11.44}$Si$_{1.56}$ hydride. To explain the pressure effects, in contrast, changes of the parameters under pressure, which are a result of the enhancement of the first-order character of the phase transition, have to be taken into account. These results indicate that either the increase or the decrease of the Curie temperature is simply a consequence of the variation of the phase volume due to the introduction of interstitial atoms or the application of a high pressure, and can be described by the Bean–Rodbell model well.

Acknowledgments

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