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Magnetic, magnetocaloric, and magnetoelastic properties of $\text{LaFe}_{11.57}\text{Si}_{1.43}\text{B}_x$ compounds

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We have studied the magnetic, magnetocaloric, and magnetoelastic properties of $\text{LaFe}_{11.57}\text{Si}_{1.43}\text{B}_x$ compounds in the concentration interval $0 < x \leq 1.64$ using magnetization and strain gauge techniques. The crystal cell parameters and Curie temperatures were found to increase linearly with increasing B concentrations up to $\sim 0.1\%$ and 9% , respectively. A positive magnetovolume anomaly of about 0.22% was observed in the vicinity of T_C . The magnetovolume coupling constant was estimated to be approximately $3 \times 10^{-3} [\mu_B/\text{Fe atom}]^{-2}$. Magnetic entropy changes at T_C slightly depended on B concentration. A hysteresis loss of about ten times smaller relative to the base compound ($x=0$) was observed for $x=1.64$. Therefore it was shown that the characteristics of the magnetocaloric effect of $\text{LaFe}_{11.57}\text{Si}_{1.43}$ can be adjusted by a change in B concentration in the $\text{LaFe}_{11.57}\text{Si}_{1.43}\text{B}_x$ system. The relative importance of the variation in the volume of crystal cell and electron concentration on T_C was discussed. © 2009 American Institute of Physics.
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I. INTRODUCTION

Ferromagnetic (FM) materials that undergo first order phase transitions (FOPTs) have drawn considerable interest due to their diverse and useful physical properties^{1–6} and therefore to their possible use in multifunctional applications. The intermetallic compound LaFe_{13} does not exist due to a positive heat of formation between La and Fe. A partial substitution of Fe by a third element is necessary to stabilize the compound in a cubic or tetragonal crystal structure.⁷ The cubic La–Fe–Si based compounds with a NaZn_{13} type of structure undergo FOPTs from a FM phase to a paramagnetic (PM) phase at the Curie temperature (T_C), and a field induced itinerant-electron metamagnetic transition from a PM to a FM phase above T_C in some Si concentration interval. Large values of magnetic entropy changes (ΔS_M) and significant magnetostriction effects were found in the vicinity of the FOPT in $\text{La}(\text{Fe},\text{Si})_{13}$ based compounds. It was reported that introducing interstitial atoms such as H, N, C, and B to $\text{La}(\text{Fe},\text{Si})_{13}$ significantly changes the phase transitions and magnetic properties of $\text{La}(\text{Fe},\text{Si})_{13}$ compounds.^{8–11} Thus the magnetic properties of $\text{La}(\text{Fe},\text{Si})_{13}$ compounds strongly depend on Si concentration and interstitial elements and can thus be controlled through adjustment of the relative concentrations. $\text{LaFe}_{11.57}\text{Si}_{1.43}$ undergoes a FOPT at $T_C \approx 200$ K.^{6,8} The variations in crystal cell volume and electron concentration are generally taken as major factors affecting the T_C of itinerant magnets. The changes in the lattice volume and conduction electron concentration are two major factors that can affect the Curie temperatures of itinerant magnets. The influence of the external and “chemical” pressure on the magnetic properties of $\text{LaFe}_{11.57}\text{Si}_{1.43}\text{H}_x$ has been studied by Lyubina *et al.*⁶ It was shown that the introduction of hydrogen in the

$\text{LaFe}_{11.57}\text{Si}_{1.43}$ compound significantly increases T_C and decreases the magnetic entropy change.^{6,8} The changes in T_C in La–Fe–Si–X ($X=\text{H},\text{C}$) compounds have been related to an increase in the crystal cell volume of these compounds.^{8,10}

In this paper we present studies of the magnetic, magnetocaloric, and magnetoelastic properties of the $\text{LaFe}_{11.57}\text{Si}_{1.43}\text{B}_x$ interstitial solid solution. Boron is chosen as an interstitial element because it contributes to the conduction band three more electrons than H and one electron less than carbon. The influence of B on the crystal structure and Curie temperature and on the characteristics of the magnetocaloric effects such as magnetic entropy changes, refrigeration capacities, and hysteresis losses of $\text{LaFe}_{11.57}\text{Si}_{1.43}$ was determined. We also observed a large change in the isotropic magnetostriction of $\approx 0.22\%$ in the vicinity of T_C and evaluated the magnetovolume coupling constant for $x=0$.

II. EXPERIMENTAL TECHNIQUES

Approximately 4 g polycrystalline $\text{LaFe}_{11.57}\text{Si}_{1.43}\text{B}_x$ ($0 \leq x \leq 1.64$) buttons were fabricated by conventional arc melting in a high purity argon atmosphere using high purity (La, Fe: 99.9%, Si: 99.9999%, and B: 99.5%) elements. For homogenization, the samples were wrapped in tantalum foil and annealed in high vacuum ($\approx 10^{-4}$ torr) for 5 days at 1000°C and slowly cooled down to room temperature. The phase purity and crystal structures were determined by powder x-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation. The relative amount of cubic phase was determined by taking the ratio of intensity of the cubic phase and the sum of the intensities of the cubic and impurity phases. The magnetic properties were measured in a temperature range of $5\text{--}400$ K, and in magnetic fields up to 5 T, using a superconducting quantum interference device magnetometer (Quantum Design, Inc.). The temperature and field induced strain measurements were carried out using strain gauge techniques in

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FIG. 1. (Color online) [(a)–(c)] Room temperature XRD patterns of $\text{LaFe}_{11.57}\text{Si}_{1.43}\text{B}_x$ and (d) lattice parameter (a) as a function of the conduction electron concentration (e/A).

magnetic fields up to 5 T. The strain was measured both parallel and perpendicular to the magnetic field direction. The Curie temperatures (T_C) were determined from the maxima of dM/dT of the $M(T, H)$ curves and were measured in an applied magnetic field of $H=0.1$ T. The saturation magnetic moments (M_S) at 5 K were estimated from the M versus H^{-1} curves by extrapolating the curves to $H^{-1}=0$. The magnetic entropy changes $\Delta S_M(T, H)$ were calculated from isothermal magnetization curves $M(H)$ using the Maxwell relation (1). The refrigeration capacity (RC) was calculated by integrating the $\Delta S_M(T, H)$ curves over the full width at half maximum using relation (2),¹²

$$\Delta S_M(T, H) = \int_0^H \left(\frac{\partial M}{\partial T} \right)_H dH, \quad (1)$$

$$\text{RC} = \int_{T_1}^{T_2} \Delta S_M dT. \quad (2)$$

III. RESULT AND DISCUSSION

The XRD patterns of $\text{LaFe}_{11.57}\text{Si}_{1.43}\text{B}_x$ for $x \leq 1.64$ indicate that the samples consist of approximately 65% of the cubic NaZn_{13} -type phase and of impurity phases consisting

FIG. 2. (Color online) (a) Temperature dependence of the magnetization $M(T)$ at $H=0.01$ T of $\text{LaFe}_{11.57}\text{Si}_{1.43}\text{B}_x$. (b) The variation in Curie temperature with conduction electron concentration (e/A). The inset of (a) shows the temperature dependence of magnetization at $H=5$ T.

of La and α -Fe and/or γ -Fe (see Fig. 1). An increase in the conduction electron concentrations (e/A), calculated using the following electron configurations of the outer shells and the corresponding number of electrons for each element as La: $5d6s^2-3$, Fe: $3d^64s^2-8$, Si: $3s^25p^2-4$, and B: $2s^22p-3$, corresponds to a linear decrease in the lattice parameter [see Fig. 1(d)]. The maximum cell volume was found to increase by about 0.07% as compared to that with $x=0$. This linear decrease in the cell parameter (a) with concentration and e/A ratio indicates that B dissolves in the crystal lattice of $\text{LaFe}_{11.57}\text{Si}_{1.43}$.

Figure 2(a) shows the typical temperature dependence of the magnetization $M(T)$ curves for $\text{LaFe}_{11.57}\text{Si}_{1.43}\text{B}_x$ compounds for an applied magnetic field of $H=0.1$ T. The sharp changes in magnetization ($T \approx 200$ K) result from the phase transitions at T_C . The relatively large magnetization above T_C can be attributed to the presence of the strong FM impurity of the α -Fe phase. An increase in the strength of the applied magnetic field during magnetization measurements results in a shift of T_C to higher temperatures [see $M(T)$ at $H=5$ T in the inset of Fig. 2(a) and Table I]. The maximum shift of the transition temperature ($\Delta T \approx 21$ K) was found for a magnetic field of 5 T (for $x=0$). It was found that a decrease in the conduction electron concentration corresponds to an increase in T_C .

In the case of $\text{LaFe}_{11.57}\text{Si}_{1.43}\text{H}_x$ (with $x=0$ and 1.64), the ratio of the change in Curie temperature to the change in lattice parameter⁶ ($\Delta T_C a / \Delta a T_C$) normalized to T_C and a for $x=0$ is approximately 60%. However, in the case of the $\text{LaFe}_{11.57}\text{Si}_{1.43}\text{B}_x$ compounds, the ratio $\Delta T_C a / \Delta a T_C$ is about 128%. Therefore we can conclude that interstitial B in

TABLE I. The phase transition temperatures, magnetic entropy changes (ΔS_M), RCs, maximum hysteresis losses, and percentages of cubic phase.

Concentration (x)	NaZn_{13} cubic structure (%)	T_C at 0.1/5 T (K)	ΔS_M ($\text{J kg}^{-1} \text{K}^{-1}$)	RC (J/kg)	Max. hysteresis loss (J/kg)	Net RC (J/kg)
0.00	67	199/220	−14	262	10	252
0.20	61	204/...	−11	232	2	230
0.75	64	207/...	−13	271	5	266
1.00	65	208/227	−15	287	12	275
1.64	56	217/232	−10	242	1	241

FIG. 3. (Color online) Isothermal magnetization (M) as a function of the magnetic field (H) for $\text{LaFe}_{11.57}\text{Si}_{1.43}\text{B}_x$ at $T=5$ K. The inset shows the saturation magnetic moment as a function of boron concentration at $T=5$ K.

$\text{LaFe}_{11.57}\text{Si}_{1.43}$ significantly changes the electronic structure compared to that of $\text{LaFe}_{11.57}\text{Si}_{1.43}$ with interstitial H.

Figure 3 shows the field dependence of the magnetization $M(H)$ of $\text{LaFe}_{11.57}\text{Si}_{1.43}\text{B}_x$ at $T=5$ K. All of the compounds were found to exhibit a FM behavior with a saturation magnetization field of about 1 T. The decrease in the saturation magnetization with B concentration is not significant (about 7% for $x=1.64$, see the inset of Fig. 3) and can be related to the presence of different amounts of impurity phases in the compounds (see Fig. 1 and Table I).

We now consider the variation in the Curie temperature of the $\text{LaFe}_{11.57}\text{Si}_{1.43}\text{B}_x$ system. In the case of a very weak itinerant ferromagnet, the ratio between M_S and T_C can be written as^{13,14} $M_S(T=0, H=0)/T_C = F[N^{(n)}(\epsilon_F)]$, where the term on the right is a function of the derivatives of the density of d -electron states (N) at the Fermi level (ϵ_F). The d -band characteristics are extremely sensitive to the composition in the case of itinerant-electron metamagnets. In other words, $N(\epsilon_F)$ changes rapidly near ϵ_F . Thus the change in conduction electron concentration in $\text{LaFe}_{11.57}\text{Si}_{1.43}\text{B}_x$ can result in a decrease in $F[N^{(n)}(\epsilon_F)]$, causing an increase in T_C .

Figure 4(a) shows typical magnetization isotherms $M(H)$ for $x=1$ in the vicinity of T_C . The magnetic field hysteresis of $M(H)$ is shown in Fig. 4(b). The magnetic hysteresis decreases with dissolving B in $\text{LaFe}_{11.57}\text{Si}_{1.43}$ and approaches zero for $x=1.64$. As a consequence the hysteresis loss, which is proportional to the enclosed area between increasing and decreasing magnetization curves, was found to be at a maximum [see the inset of Fig. 4(b)] for $x=1$ and at a minimum for $x=1.64$ (see in Table I). Thus, the magnetization process becomes more reversible with respect to the magnetic field with increasing interstitial B concentration. The reduction in magnetic hysteresis is a favorable characteristic regarding magnetic refrigeration applications.

The magnetic entropy changes (ΔS_M) have been estimated from the isothermal magnetization curves using the Maxwell relation (1). Typical ΔS_M curves as a function of temperature are shown in Fig. 5 for $x=1$. The maximum values of ΔS_M at $H=5$ T for the rest of samples are reported in Table I. An increase in the concentration of interstitial B atoms results in a shift of the maximum of ΔS_M to higher temperature following a similar change in the Curie temperature. The ΔS_M remains nearly the same as that of the parent

FIG. 4. (Color online) (a) Isothermal magnetization curves $M(H)$ for $\text{LaFe}_{11.57}\text{Si}_{1.43}\text{B}_x$ in the vicinity of the T_C for $x=1$ and (b) the hysteresis loops in the vicinity of the T_C . The arrows in (b) show the hysteresis loops for increasing and decreasing magnetic fields. The inset of (b) shows the variation in hysteresis loss as a function of temperature in the vicinity of T_C for $x=1$.

compounds for $x \leq 1$ and decreases to $\Delta S_M = -10 \text{ J kg}^{-1} \text{ K}^{-1}$ for $x=1.64$ (for a field change of 5 T). Although not shown here, ΔS_M increases almost linearly with ΔH and does not saturate for $\Delta H=5$ T.

The RC, which is a useful parameter that is used to quantify the magnetocaloric properties, was calculated from relation (2). It was found to vary from 287 to 232 J/kg with the variation in B concentration. The ΔS_M and RC values for different B concentrations are presented in Table I. Magnetic hysteresis [see Fig. 4(b)] results in thermal losses, which opposes the RC, and is therefore an unwanted characteristic in magnetocaloric materials.¹² The net RC was calculated by subtracting the maximum hysteresis loss at each temperature through the relevant transitions. The maximum net RC was found to be 275 J/kg for $x=1$ (see in Table I).

Figure 6 shows the temperature and field dependent strain measurement both parallel [$\epsilon_{\parallel}(T, H)$] and perpendicular

FIG. 5. (Color online) (a) Magnetic entropy change (ΔS_M) of $\text{LaFe}_{11.57}\text{Si}_{1.43}\text{B}_x$ with temperature in the vicinity of T_C for $x=1$.

FIG. 6. (Color online) (a) Temperature dependence of strain for parallel (triangles) and perpendicular (circles) to the direction of applied field at $H=0$ T and (b) field dependence of the strain for parallel and perpendicular fields. Arrows represent the direction of the temperature and field.

lar $[\varepsilon_{\perp}(T, H)]$ to external magnetic fields up to 5 T. It was found that the strains in both field directions were similar $[\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ as a function of temperature for $H=0$ are shown in Fig. 6(a)]. The strain increases almost linearly for $T < T_C$ and then shows a sharp jump at T_C . The observed temperature hysteresis in the strain is indicative of a first order transition. The strain increased with increasing magnetic field up to $H=5$ T. When the magnetic field was reduced from 5 T, the strain decreased, and the total irreversible strain was observed to be -0.17% for both positive and negative field directions at $T=205$ K. Above 205 K, a completely reversible positive value of the strain (0.22%) was observed for both parallel and perpendicular magnetic field directions [see Fig. 6(b)]. This value of the strain is similar to that found in $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}$.¹

Figure 7(a) shows the strain [obtained from $\varepsilon(H)$] as a function of M [obtained from $M(H)$] for $\text{LaFe}_{11.57}\text{Si}_{1.43}$. It was found that the volume magnetostriction $\omega_S = \varepsilon_{\parallel} + 2\varepsilon_{\perp} \approx 3\varepsilon_{\parallel}$ is proportional to the square of the magnetization, starting with a saturating magnetic field [see Fig. 7(b)].

FIG. 7. (Color online) (a) Variation in the strain as a function of magnetization obtained from the $M(H)$ curve at $T=206$ K and (b) the variation of volume magnetostriction as a function of the square of the magnetization.

Magnetic ordering of itinerant d -electrons is accompanied by a positive magnetovolume anomaly (ω_S),¹⁵ which can be written as

$$\omega_S(T) = [V_{\text{fer}}(T) - V_{\text{para}}(T)]/V_{\text{para}} = \delta V/V = kCM^2 \\ = n_{dd}M^2 \approx 3\varepsilon(T)_{\parallel, \perp}$$

or

$$\omega_S(H) = \varepsilon_{\parallel} + 2\varepsilon_{\perp} = n_{dd}M^2, \quad (3)$$

where V_{fer} and V_{para} are the crystal cell volumes in the PM and FM states, respectively, n_{dd} is the magnetovolume coupling constant, and M is the magnetic moment of the d -electron subsystem. Using relation (3), it is possible to estimate the magnetovolume constant of the $\text{LaFe}_{11.57}\text{Si}_{1.43}$ compound from $\varepsilon(T, H)$ and $M(T, H)$ measurements. The estimated magnetovolume coupling constant from Figs. 7(b) and 6(a) and the inset of Fig. 2(a) was found to be $n_{dd} \approx 3 \times 10^{-3} (\mu_B/\text{Fe atom})^{-2}$, which is the same order of magnitude that was found for other itinerant-electron metamagnets (see Ref. 16 and references therein).

IV. CONCLUSIONS

We have investigated the structural, magnetic, magneto-caloric, and magnetostriction properties of $\text{LaFe}_{11.57}\text{Si}_{1.43}\text{B}_x$ compounds. It was found that boron can be dissolved in the crystal lattice of $\text{LaFe}_{11.57}\text{Si}_{1.43}$ for $x \leq 1.64$. The Curie temperature of $\text{LaFe}_{11.57}\text{Si}_{1.43}\text{B}_x$ increases with an increase in the cell volume about two times more rapidly than that observed in $\text{LaFe}_{11.57}\text{Si}_{1.43}\text{H}_x$. Such behavior is attributed to a change in the density of d -electron states at the Fermi level as a result of the change in the conduction electron concentration in the case of B and H interstitial solid solutions. The volume (isotropic) magnetostriction was found to depend on the square of the magnetization, which is related to the change in the d -electron magnetic moment. A large value of magnetostriction of about 0.22% in the vicinity of T_C for a magnetic field change of 5 T was found for $x=0$. This magnetostriction is attributed to a FM FOPT driven by itinerant electrons. The magnetovolume coupling constant of $n_{dd} \approx 3 \times 10^{-3} (\mu_B/\text{Fe atom})^{-2}$ of $\text{LaFe}_{11.57}\text{Si}_{1.43}$ has been estimated from magnetization and strain measurements. The maximum value of $\Delta S_M = -15 \text{ J kg}^{-1} \text{ K}^{-1}$ was found for $x=1$ at $T=208$ K. The hysteresis loss was found to decrease with B concentration. It is hoped that these results will encourage further scientific exploration of these systems and the development of multifunctional applications that utilize them.

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