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

J.C Debnath
ISEM

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

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

Stewart J. Campbell
UNSW, stewart.campbell@adfa.edu.au

See next page for additional authors

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Authors
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Reduction of hysteresis losses in the magnetic refrigerant $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}$ by the addition of boron

P. Shamba,[1,a)] J. C. Debnath,[1] R. Zeng,[1] J. L. Wang,[1,2,3] S. J. Campbell,[2] S. J. Kennedy,[3] and S. X. Dou[1]
[1]*Institute for Superconducting and Electronic Materials, University of Wollongong, Wollongong, NSW 2522, Australia*
[2]*School of Physical, Environmental and Mathematical Sciences, University of New South Wales, Australian Defence Force Academy, Canberra, ACT 2600, Australia*
[3]*Bragg Institute, Australian Nuclear Science and Technology Organization, Lucas Heights, NSW 2234, Australia*

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In an effort to improve the magnetocaloric effects of the $NaZn_{13}$-type $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}$ compound, the effect of boron doping on the magnetic properties and magnetocaloric properties has been investigated. The magnetic entropy change (ΔS_M) for the $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}$ compound, obtained for a field change of 0–5 T using the Maxwell relation exhibits a spike and appears to be overestimated and is thus corrected by using the Clausius-Clapeyron equation (CC). The ΔS_M determined from the CC equation is estimated to be 19.6 J $kg^{-1}K^{-1}$. However, large hysteretic losses which are detrimental to the magnetic refrigeration efficiency occur in the same temperature range. In this work, we report a significant reduction in hysteretic losses by doping the $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}$ compound with a small amount of boron to obtain $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_x$ compounds. The hysteresis loss decreases from 131.5 to 8.1 J kg^{-1} when x increases from 0 to 0.3, while ΔS_M, obtained for a field change of 0–5 T, varies from 19.6 to 15.9 J $kg^{-1}K^{-1}$. This also simultaneously shifts the T_C from 174 to 184 K and significantly improves the effective refrigerant capacity (RC_{eff}) of the material from 164 to 305 J kg^{-1}. *© 2011 American Institute of Physics.* [doi:10.1063/1.3565401]

Amid growing concerns regarding global warming and the ever-increasing energy consumption which is being worsened by the current use of conventional vapor-compression refrigeration technologies, scientists have expended a great amount of research effort to find magnetic materials with a large ambient magnetic entropy change which can be used in magnetic refrigeration (MR) as an alternative cooling technology.[1–5] Magnetic materials having a first order magnetic phase transition (FOMT), exhibit large magnetocaloric effects (MCEs) and are thus suitable candidates for magnetic refrigerants.[6–8] $LaFe_{13-x}Si_x$ compounds with a cubic $NaZn_{13}$-type structure are one of the most attractive because of their considerably large MCEs and low cost. These large MCEs in $LaFe_{13-x}Si_x$ result from the itinerant-electron metamagnetic (IEM) transition in the vicinity of the first-order phase transition temperature.[9–11] However, the first order transition is usually accompanied by a considerable level of thermal and magnetic hysteresis, bringing about hysteresis loss which is detrimental to the refrigerant capacity. To date, several studies have been done to reduce or eliminate hysteresis in $LaFe_{13-x}Si_x$ based alloys.[12–15] These include a study by Lyubina *et al.* in 2008 where melt spinning was shown to significantly reduce hysteresis in $LaFe_{13-x}Si_x$ based alloys compared to the bulk material.[16] However, the most common method of reducing the hysteretic losses in $LaFe_{13-x}Si_x$ based compounds is by the addition of substitutional or interstitial atoms.[12–15,17]

a)Author to whom correspondence should be addressed. Electronic mail: ps807@uow.edu.au.

As such, the control of hysteresis due to the first order transition is imperative for the improvement in the performance of magnetic refrigerants. In view of this, we have studied the magnetic and magnetocaloric properties of boron doped $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}$ with the main aim of investigating the effect of boron doping on the hysteresis and consequently, the refrigerant capacity of this material system.

Ingots of polycrystalline alloys with nominal compositions $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_x$ ($x = 0$, 0.1, and 0.3) were prepared by arc-melting appropriate amounts of the high purity constituent elements under a high purity argon atmosphere in a water cooled copper crucible. The purities of the starting materials were 99.9% for La, Si, and Fe, 99.99% for Ce and 99.999% for B. Excess La and Ce (10 at. %) were used to compensate for the weight loss during the arc melting. During the arc melting process, each ingot was turned over and remelted several times to ensure its homogeneity. The resulting ingots were wrapped in tantalum foil, annealed at 1323 K for 14 days in an evacuated quartz tube to improve the crystallization of the samples and then quenched in water. The crystal structure of the samples was determined by room temperature powder x-ray diffraction (XRD) with Cu $K\alpha$ radiation. The magnetization was carried out using the vibration sample magnetometer option of a Quantum Design 14 T physical property measurement system in the temperature range of 140–240 K at applied fields of up to 5 T.

The XRD results indicate that all the alloys crystallized in a single phase with the $NaZn_{13}$-type cubic structure. Figure 1 shows the temperature dependencies of the magnetization measured in the heating and cooling processes under a low magnetic field of 0.02 T and a temperature range from 140 - 220 K of $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_x$ samples with $x = 0$, 0.1, and 0.3. The Curie temperature, T_C, which is defined as the temperature at which the dM/dT of the heating M-T curves is a minimum, is found to increase with an increase in boron content from 174,182, and finally to 184 K for $x = 0$, 0.1, and 0.3, respectively. This increase in T_C with increasing boron doping, x, can be attributed to the lattice expansion caused by the introduction of interstitial boron atoms.[13] In our study, the M-T curve for the undoped sample shows a considerable thermal hysteresis (17.4 K) which indicates the first-order nature of this transition. However, upon increasing the boron doping, x, it is evident from Fig. 1 that the thermal hysteresis is reduced to 12.7 and 11.7 K for $x = 0.1$ and 0.3, respectively.

Figure 2 displays the magnetization curves for the $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_x$ ($x = 0$, 0.1, and 0.3) alloys which show a field induced metamagnetic transition. The first abrupt increase of magnetization marks the contribution of the FM phase, while the subsequent steplike variation signifies the field-induced metamagnetic transition of the PM phase to the FM phase with the inflection point of this steplike transitional region being the critical field value, H_C. For samples with $x = 0$, 0.1, and 0.3, H_C linearly depends upon temperature with a rate of 0.21, 0.20, and 0.17 T/K, respectively. A similar trend was observed in $Mn_{0.99}Fe_{0.01}As$.[18] Furthermore, the M-H curves measured under increasing and decreasing fields exhibit significant magnetic hysteresis loops for $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_x$ with $x = 0$, 0.1, and 0.3. It can be clearly seen that the hysteresis becomes smaller with an increase in boron doping, x.

Figure 3 shows the temperature dependence of the hysteresis loss, defined as the area enclosed by the ascending and descending branches of the magnetization curve. The maximal hysteresis losses around T_C are 131.5, 30.4, and 8.1 J kg^{-1} measured under a 5 T field for $x = 0$, 0.1, and 0.3, respectively. The inset shows the maximum hysteresis loss measured under a 2 T field, which is also found to decrease with an increase in x. This reduction in hysteresis losses is attributed to the weakening of the field induced FOMT from the paramagnetic to the ferromagnetic state due to the addition of boron. In an isothermal process, the magnetic entropy change of the materials can be derived from the Maxwell relation which is shown below

$$\Delta S_M(T, p, \Delta H)_{\Delta H, p} = \int_{H_1}^{H_2} \left[\frac{\partial M(T, p, H)}{\partial T} \right]_{H,p} dH. \quad (1)$$

The maximum ΔS_M for $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_x$ samples with $x = 0$, 0.1, and 0.3 range from 72.2–16.4 J $kg^{-1}K^{-1}$ measured under a field of 5 T and are shown in Fig. 4. The ΔS_M for the pure $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}$ compound derived from the Maxwell relation is in good agreement with Ref. 17. However, the presence of the ΔS_M spikes as shown in Fig. 4 are a reason for concern as their presence implies that the ΔS_M predicted by the Maxwell relation could be erroneous. Previously, Pecharsky *et al.*,[19] showed that no ΔS spikes are expected for a normal first order transition. Thus ΔS_M is recalculated using the CC equation which is shown below

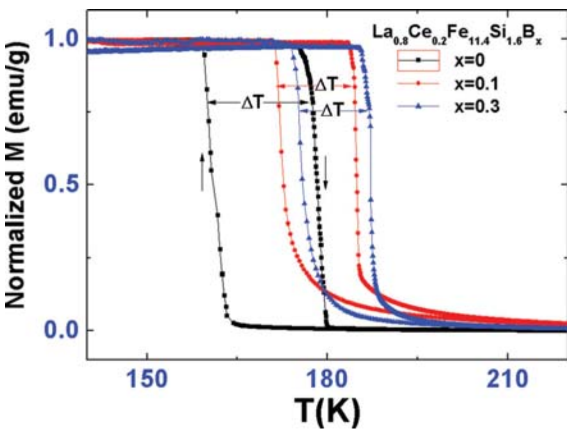

FIG. 1. (Color online) Temperature dependence of the magnetization measured on heating and cooling in a magnetic field of 0.02 T for $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_x$ for x values of 0, 0.1, and 0.3.

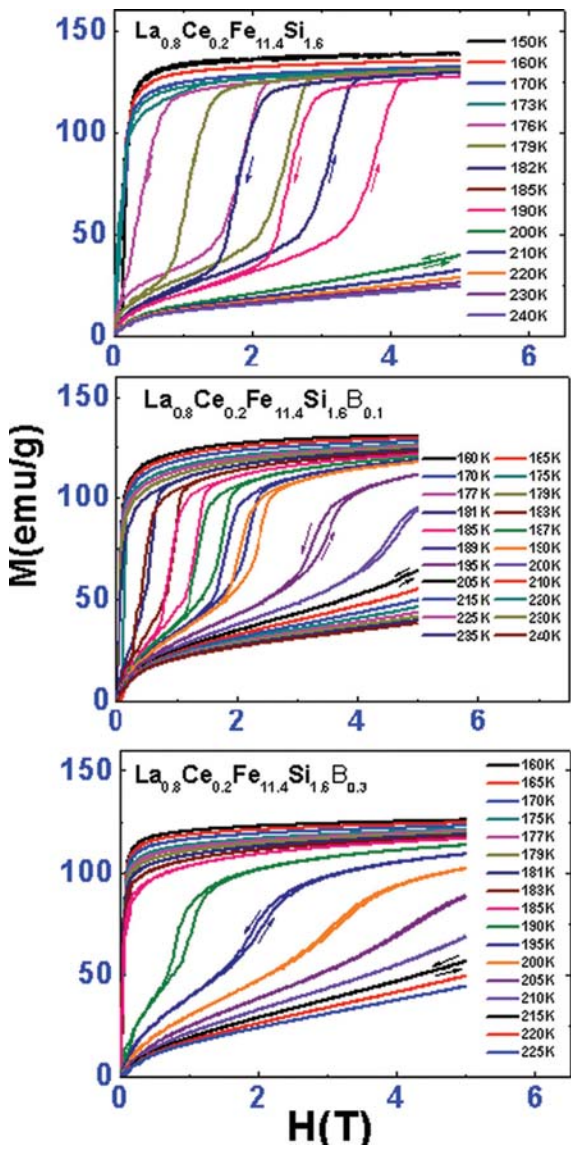

FIG. 2. (Color online) Magnetization isotherms of $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_x$ for x values of 0, 0.1, and 0.3, measured in the field ascending and field descending processes.

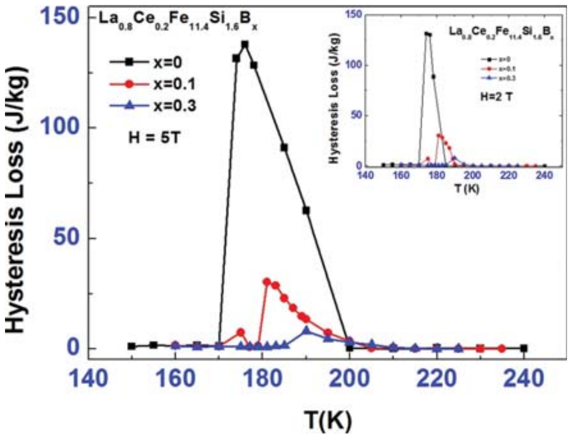

FIG. 3. (Color online) Temperature dependence of the hysteresis loss of $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_x$ for x values of 0, 0.1, and 0.3 measured at 2 and 5 T.

$$\Delta S = -\Delta M \frac{dH_c}{dT}, \tag{2}$$

where ΔM is the difference of magnetization between the low and high field parts in the M-H curves shown in Fig. 2.

Thus, Fig. 4 shows a comparison of the ΔS_M calculated using the CC equation and the ΔS_M predicted by the Maxwell relation. The maximum ΔS_M calculated using the CC equation for the $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_x$ samples with $x = 0$, 0.1, and 0.3 are 20.8, 12.4, and 8.9 J $kg^{-1}K^{-1}$ respectively, and similar to what Balli *et al.*[18] observed in $Mn_{0.99}Fe_{0.01}As$, the ΔS_M peaks for these samples derived from the CC equation are centered at slightly higher temperatures than the MCE peaks derived from the Maxwell relation.

The efficiency of a solid-state cooling device is determined by the magnitude of the refrigerant capacity, RC which is calculated by numerically integrating the area under the ΔS_M-T curve, with the integration limits being the temperatures at half maximum of the peak. Tabulated values of the RC as a function of B field at 5 T calculated using ΔS_M

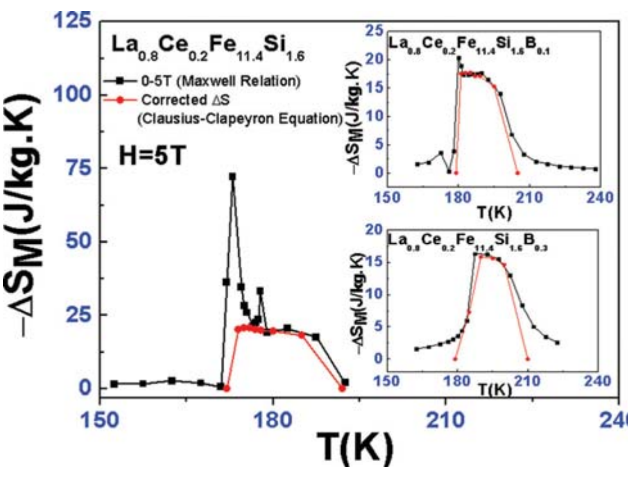

FIG. 4. (Color online) Comparison of the isothermal magnetic entropy change of $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_x$ for x values of 0, 0.1, and 0.3 measured at 5 T calculated from the Maxwell relation and the CC equation.

TABLE I. Tabulated values of the refrigerant capacity RC (MR), RC (CC), and the effective refrigerant capacity RC_{eff} (MR) and RC_{eff} (CC), at 5T for $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_x$ for x values of 0, 0.1, and 0.3.

Sample	H	RC (MR)	RC (CC)	RC_{eff} (MR)	RC_{eff} (CC)
$La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}$	5	176.6	295.5	45.1	164
$La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_{0.1}$	5	437.2	335.4	406.8	305
$La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_{0.3}$	5	461.8	306.1	453.7	298

obtained using the Maxwell relation and the Clausius-Clapeyron equation, RC (MR) and RC (CC), respectively, are shown in Table I. RC (MR) and RC (CC) increase with an increase in boron doping, x. From Table I, the calculated RC (MR) is significantly higher than the RC (CC) due to the fact that in calculating RC (MR), an overestimated value of ΔSM, obtained from the Maxwell relation is used. Thus, RC (CC) gives a reasonable estimate of the refrigerant capacity. Although $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_x$ compounds exhibit high RC values, they also have a large hysteresis loss, demonstrated in Fig. 3, which reduces the MCE of the material.

By subtracting the hysteresis loss from the calculated RC (MR) and RC (CC), we obtained the effective refrigerant capacities RC_{eff} (MR)and RC_{eff} (CC) which are shown in Table I, calculated for magnetic field values of 5 T. As boron doping, x varies from 0 to 0.3, both the RC_{eff} (MR) and RC_{eff} (CC) show a similar trend to that observed in the RC (MR) and RC (CC), with RC_{eff} (CC) being a reasonable estimate of the effective refrigerant capacity. These results indicate that the introduction of interstitial boron atoms significantly improves the cooling capacity of the $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}$ material system.

The determination of ΔS_M for $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}B_x$ compounds using the Clausius-Clapeyron equation yields reasonable estimates of the MCE in these compounds. Our results demonstrate that the hysteresis behavior of a material is critical in evaluating its potential as a functional magnetic refrigerant.

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