

## Volume dependence of the magnetic coupling in $\text{LaFe}_{13-x}\text{Si}_x$ based compounds

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The effects of pressure and hydrogenation, the former causes a lattice contraction while the latter causes an expansion of the sample, have been systematically studied for  $\text{LaFe}_{13-x}\text{Si}_x$  ( $x=1.3-2.1$ ). It is found that the typical change of the Curie temperature is  $\sim 150$  K when  $\sim 1.6$  H/f.u. is absorbed and  $\sim -106$  K as the pressure sweeps from 0 to 1 GPa. One of the most remarkable results of the present work is the presence of a universal relation between Curie temperature and phase volume. The former linearly grows with the increase of lattice constant ( $\sim 1510$  K/Å), irrespective of how the phase volume is modified. This result implies the exclusive dependence of the magnetic coupling in  $\text{LaFe}_{13-x}\text{Si}_x$  on the Fe-Fe distances and the interstitial hydrogen does not affect the electronic structure of the compounds. © 2008 American Institute of Physics.

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Intermetallics  $\text{LaFe}_{13-x}\text{Si}_x$  (LFS) have attracted much attention in recent years because of their giant magnetocaloric effect (MCE),<sup>1-3</sup> based on which, a promising refrigeration technique could be developed. In addition to significant MCE, the most remarkable feature of LFS is the strong dependence of its Curie temperature ( $T_C$ ) on element doping or external perturbations such as magnetic field and pressure. It has been reported that a pressure of 1 GPa reduces  $T_C$  by  $\sim 100$  K,<sup>4</sup> whereas a magnetic field of 5 T lifts  $T_C$  by  $\sim 25$  K. It is the variation of  $T_C$  under applied field that yields the MCE. Compared with magnetic field and pressure, effects of interstitial hydrogen or carbon are much stronger,<sup>2</sup> and the presence of  $\delta=1.5$  hydrogen in  $\text{LaFe}_{11.44}\text{Si}_{1.56}\text{H}_\delta$  can lift  $T_C$  by  $\sim 130$  K.<sup>3</sup> Replacing Fe by other elements such as Si or Co produces similar effects.

It is obvious that the phase volume (Fe-Fe distance), the number of Fe-Fe pairs, and even the electronic structure of LFS, either of which may affect  $T_C$ , could be affected by element substitution or external field/pressure. Noting the close relation between MCE and the field sensitivity of  $T_C$ , to find out the key factors that govern the magnetic coupling could be helpful for improving MCE. Although the effects of element doping and high pressure have been extensively studied before, a comprehensive analysis that can lead to a deep understanding of the magnetic behavior of LFS is still lacking. Based on this consideration, in this letter, we will perform a systematic study on the effects of pressure and hydrogenation, the former causes a volume contraction, while the latter causes an expansion of the samples. The

most remarkable result of the present work is the presence of a universal relation between Curie temperature and phase volume. This result implies that the magnetic coupling is exclusively determined by the distance between Fe atoms when the content of Fe is fixed.

LFS compounds with  $x=1.3-2.1$  were prepared following the procedures described elsewhere.<sup>5</sup> The resultant LFS samples were first hydrogenized in  $\text{H}_2$  gas with a pressure of 5 MPa at 150 °C for  $\sim 5$  h, then annealed in high vacuum ( $\sim 5 \times 10^{-4}$  Pa) at 250 °C for different durations to obtain the hydrides with different hydrogen contents.

Phase purity and crystal structure of the samples were studied by x-ray diffraction (XRD) conducted by a Rigaku diffractometer with a rotating anode and  $\text{Cu } K\alpha$  radiation. A superconducting quantum interference device magnetometer and a vibration sample magnetometer were used for the magnetic measurements below and above 300 K, respectively. Details for the magnetic measurements under high pressure have been described in Ref. 5. The structures under high pressure were analyzed by the XRD at the beamline 11-ID-C (Advanced Photon Source, Argon National Laboratory) using synchrotron radiation of the energy of 115.227 keV ( $\lambda=0.1076$  Å).

As confirmed by the XRD analysis, the samples thus obtained are of single phase with the cubic  $\text{NaZn}_{13}$ -type structures. The introduction of interstitial hydrogen causes a considerable lattice expansion as signified by the low-angle shift of the XRD peaks, though the crystal structure remains unchanged. As a representative, we show in Fig. 1 the typical XRD spectra for the sample of  $x=1.5$ . A simple analysis indicates that the lattice constant increases from  $\sim 11.468$  to  $\sim 11.601$  Å upon hydrogenating, with the rela-

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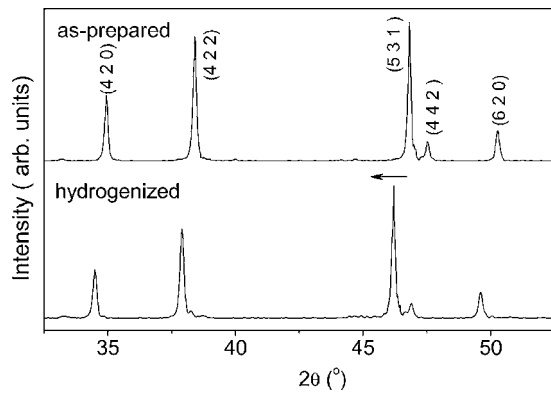


FIG. 1. XRD patterns of the as-prepared and hydrogenised  $\text{LaFe}_{11.5}\text{Si}_{1.5}$  collected at room temperature. Arrow in the figure marks the direction along which the XRD peaks shift.

tive volume change of  $\sim 3.4\%$ . As will be seen later, the incorporation of hydrogen pushes  $T_C$  of up to  $\sim 356$  K. This implies that the detected volume expansion is caused by interstitial hydrogen and the ferromagnetic-paramagnetic (FM-PM) transition, the FM state exhibits a larger phase volume than the PM one. As expected, hydrogen release leads to a high-angle shift of the XRD peaks (not shown). Therefore, by tuning the temperature and duration of the vacuum annealing, the content of hydrogen can be well regulated.

Figure 2 exemplifies the temperature-dependent magnetization ( $M$ ) of the  $\text{LaFe}_{11.5}\text{Si}_{1.5}$  hydrides measured under a field of 50 mT (top panel). It demonstrates the strong effects of interstitial hydrogen on magnetic behaviors. The Curie temperature, defined by the temperature corresponding to the rigid corner of the  $M$ - $T$  curve, increases from  $\sim 194$  to  $\sim 356$  K after hydrogenation, while progressively decreases

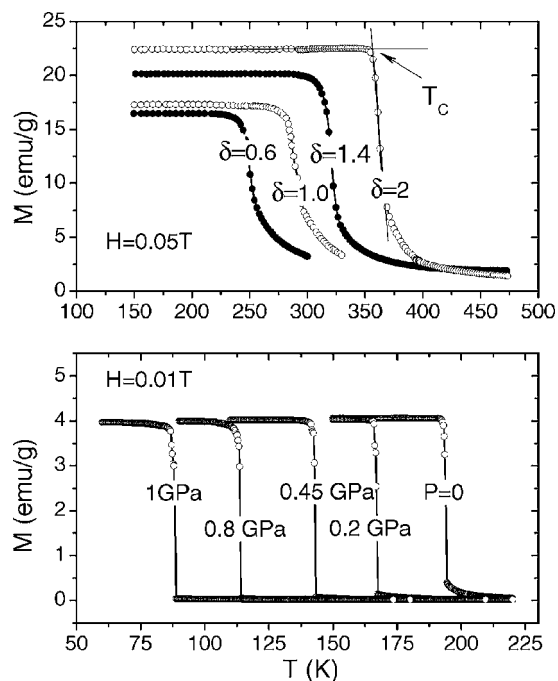


FIG. 2. Thermomagnetic curves of the  $\text{LaFe}_{11.5}\text{Si}_{1.5}\text{H}_\delta$  hydrides with different H content measured under the field of 0.05 T (top panel) and the thermomagnetic curves of  $\text{LaFe}_{11.5}\text{Si}_{1.5}$  under different pressures measured under a field of 0.01 T (bottom panel). Content of interstitial hydrogen is obtained by comparing the variation of Curie temperature of present samples with that of Ref. 3, where  $\delta$  has been explicitly given. Solid lines are guides for the eyes.

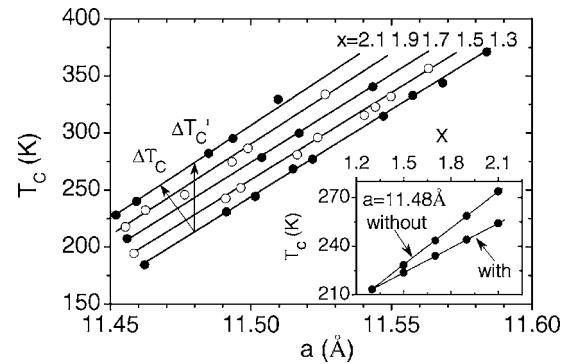


FIG. 3. Curie temperature as a function of lattice parameter for the hydrides with different Si contents. The inset plot shows the Curie temperatures as a function of Si content with and without volume effect ( $a=11.48$  Å).  $\Delta T_C$  and  $\Delta T'_C$  denote the results with and without volume change, respectively. Solid lines are guides for the eyes.

with the release of hydrogen. In contrast, high pressure depresses  $T_C$ , and a  $T_C$  drop of  $\sim 106$  K is produced by a pressure of 1 GPa (bottom panel of Fig. 2). Similar behaviors are observed in other samples with different Si contents.

It is obvious that the direct impact of high pressure or interstitial hydrogen is on the phase volume. To get a deep insight into the underlying physics of volume effects, it would be helpful to check the relation between  $T_C$  and phase volume. Based on the XRD data collected at the ambient temperature ( $\sim 296$  K), the lattice constant at  $T_C$  (PM phase) can be derived following the relation  $a(T_C)=a_0-\beta(296-T_C)$  for  $T_C < 296$  K and  $a(T_C)=a_0+\beta(T_C-296)-\Delta a$  for  $T_C > 296$  K, where  $a_0$  is the lattice constant at  $\sim 296$  K,  $\Delta a$  is the lattice expansion accompanying the FM-PM transition, and  $\beta/a_0 \approx 8.2 \times 10^{-6} \text{ K}^{-1}$  is the linear expansivity of LFS.<sup>6</sup>  $\Delta a$  can be derived from the rigid shift of the  $T_C$ - $a_0$  curve along the  $a_0$  axis when  $T_C$  exceeds 296 K and it is found to be  $\sim 0.044$  Å, essentially independent of Si content.

As shown in Fig. 3 a linear increase of  $T_C$  with  $a$  at a rate of  $\sim 1510 \text{ K}/\text{Å}$  is observed for all of the samples investigated. The increase in Si content leads to a parallel shift of the  $T_C$ - $a$  curve. This implies that the magnetic coupling varies in a similar manner as the Fe-Fe distance changes, irrespective of the content of Si. As is well known, two effects can be produced by replacing Fe with Si. The first one is the lattice contraction and the second one is the hybridization of the  $s$  orbital of Si and the  $d$  orbital of Fe. The former leads to a decrease while the latter leads to an increase of  $T_C$ . The two effects always appear simultaneously and, as a result, cannot be distinguished from each other. It is easy to see that the data in the  $T_C$ - $a$  curves corresponding to the same lattice constant actually mark the variation of  $T_C$  with  $x$ , which is an effect simply due to the dilution of Fe by Si, without volume effect. The inset plot in Fig. 3 compares the change of the Curie temperatures with and without volume change. This result is important in the sense that it is the base for any further analyses of the effects of Fe dilution.

To get the knowledge about the magnetic coupling in LFS, the effects of lattice contraction are further studied. To compare with the results of hydrogenation, information on pressure induced volume change is required. The crystal structure of  $\text{LaFe}_{11.5}\text{Si}_{1.5}$  was analyzed by synchrotron radiation XRD conducted under the pressures of up to 4.1 GPa. Thus, the compressibility obtained is  $\kappa = -V^{-1}dV/dP \approx 8.639 \times 10^{-3} \text{ GPa}^{-1}$ , where  $P$  is pressure and  $V$  is the vol-

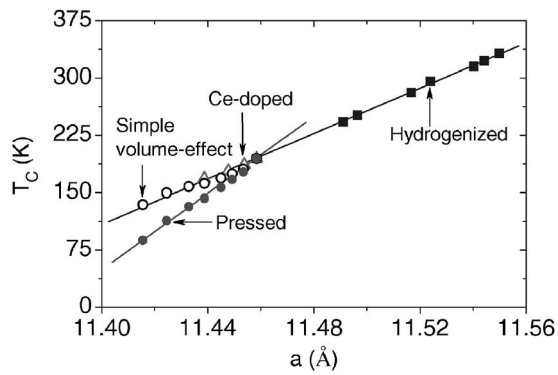


FIG. 4. Curie temperature as a function of lattice constant of the hydrogenized and pressed  $\text{LaFe}_{11.5}\text{Si}_{1.5}$  and Ce-doped  $\text{LaFe}_{11.5}\text{Si}_{1.5}$ . The open circles show the pure volume effects while the solid circles show the as-detected  $T_C$  under pressures. Solid lines are guides for the eyes.

ume. The volume under high pressure has the form  $V = V_0(1 - \kappa P)$  ( $V_0$ , the volume under ambient pressure). Based on these results, the  $T_C$ - $a$  relation under pressures can be obtained (solid circles in Fig. 4). Results of hydrogenation and Ce doping for  $\text{La}_{1-y}\text{Ce}_y\text{Fe}_{11.5}\text{Si}_{1.5}$  ( $y=0-0.3$ ) (Ref. 7) are also presented for comparison (hollow triangles in Fig. 4). It can be seen that the slope of the  $T_C$ - $a$  relations is essentially the same in the cases of hydrogenating and Ce substitution  $\sim 1510 \text{ K}/\text{\AA}$  but considerably large under pressures  $\sim 2450 \text{ K}/\text{\AA}$ .

In fact, two effects on  $T_C$  can be produced by high pressures. The first one is the shrinkage of phase volume, which affects the magnetic coupling by modifying the Fe-Fe distance and the second one is the stabilization of the PM state due to the extra reduction of free energy of the form of  $P\Delta V$  compared with the FM state, where  $\Delta V$  is the volume difference of the two states. To compare with the results of hydrogenating, however, only the effects arising from the change of Fe-Fe distance should be considered. It has been known that a field of 1 T shifts  $T_C$  by  $H\Delta M/\Delta S \approx 4.2 \text{ K}$ , where  $\Delta S$  and  $\Delta M$  are the entropy and magnetization changes, respectively, as  $\text{LaFe}_{11.5}\text{Si}_{1.5}$  transits from the FM to the PM state. Noting the fact that magnetic field and pressure affect the free energy via  $HM$  and  $PV$ , respectively, the excessive reduction of  $T_C$  produced by pressure can be expressed as  $\Delta T_C \approx 4.2(P\Delta V/H\Delta M) = 0.0739PV(\Delta M/M_S)^2/H\Delta M$  ( $H=1 \text{ T}$ ) based on the simple relation  $\Delta V/V \approx 0.0176(\Delta M/M_S)^2$ , derived from the data in Ref. 6, where  $\Delta V$  and  $\Delta M$  are the volume and magnetization changes, respectively, of the compound at  $T_C$  and  $M_S$  is the saturation magnetization. Using the  $\Delta M$  data under different pressures extracted from the data in Ref. 5,  $\Delta T_C$  can be directly calculated. After compensating the extra  $\Delta T_C$ , we obtain the variation of  $T_C$  simply produced by the change of Fe-Fe distance (hollow circles in Fig. 4). It is clear that with the decrease of pressure or the increase of hydrogen content, the phase volume expands monotonously. The minimal and maximal lattice constants of the PM phase near  $T_C$  are  $\sim 11.416$  and  $\sim 11.563 \text{ \AA}$ , corresponding to  $P=1 \text{ GPa}$  and  $\delta \approx 2$ , respectively. The most remarkable result of the present work is the universal relation between  $T_C$  and  $a$ ;  $T_C$  increases linearly with  $a$  at the rate of  $\sim 1510 \text{ K}/\text{\AA}$ , irrespective of how the phase volume is modified.

The magnetic exchange in LFS could be mainly determined by the Fe-Fe interaction, and the rare-earth atom ex-

ists as a support to the crystal structure. A Rietveld analysis of the XRD data has been performed for the sample  $\text{LaFe}_{11.5}\text{Si}_{1.5}$  and its hydrides (relevant results will be published separately). It reveals that the Fe-Fe bond experiences an expansion on hydrogenation, especially the one that joins two adjacent  $(\text{Fe}/\text{Si})_{13}$  icosahedrons. There is a linear relation between bond length and lattice constant. The average Fe-Fe bond length increases from  $\sim 2.518$  to  $\sim 2.539 \text{ \AA}$  when the lattice constant grows from  $\sim 11.468$  to  $\sim 11.601 \text{ \AA}$ . It has been well established that the Fe-Fe interaction undergoes a monotonic increase with the Fe-Fe distance when the latter varies in the range from 2.45 to 2.6  $\text{\AA}$ .<sup>8</sup> In this picture, the lattice expansion due to the incorporation of hydrogen will enhance the magnetic coupling between Fe atoms, thus, stabilize the FM phase. In fact, an increase in the dispersion coefficient of spin waves has been observed by Fujita and Fukamichi.<sup>9</sup> According to the standard thermodynamics theory, the free energy of the FM state will be equal to that of the PM state at  $T_C$  for a first-order phase transition. A direct calculation shows  $T_C = (U_{\text{PM}} - U_{\text{FM}})/(S_{\text{PM}} - S_{\text{FM}})$  for  $P=0$  and  $H=0$ , where  $U$  and  $S$  represent the internal energy and entropy of the compounds, respectively. The enhancement of magnetic coupling implies the reduction of  $U_{\text{FM}}$ , thus, the increase of  $T_C$ . On the contrary, the pressure-produced decrease of the exchange interaction leads to the reduction of  $T_C$ . These explain the variation of  $T_C$  with the change of phase volume.  $T_C$  is expected to be sensitive to the change of the magnetic coupling for a system with a high saturation magnetization because the exchange energy is proportional to  $M_S^2$  in the mean field frame.

It has been argued that interstitial hydrogen can affect the electronic structure of the compound by contributing an extra electron. In contrast, high pressure simply causes a lattice contraction, without any extra disturbances. The similar  $T_C$ - $a$  relations in these two cases suggest the dominative role of the Fe-Fe distance in governing the magnetic coupling of LFS, and the electronic structure is not affected by interstitial hydrogen. This may also explain why interstitial hydrogen does not affect the first-order character of the magnetic transition.

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