Volume dependence of the magnetic coupling in LaFe_{13-x}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 LaFe_{13-x}Si_x (x = 1.3–2.1). It is found that the typical change of the Curie temperature is ~150 K when ~1.6 H/f.u. is absorbed and ~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 (~1510 K/Å), irrespective of how the phase volume is modified. This result implies the exclusive dependence of the magnetic coupling in LaFe_{13-x}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 LaFe_{13-x}Si_x (LFS) have attracted much attention in recent years because of their giant magnetocaloric effect (MCE).¹–³ 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 ~100 K,⁴ whereas a magnetic field of 5 T lifts T_C by ~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,² and the presence of δ=1.5 hydrogen in LaFe_{11.44}Si_{1.56}H_δ can lift T_C by ~130 K.³ 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.⁵ The resultant LFS samples were first hydrogenized in H_2 gas with a pressure of 5 MPa at 150 °C for ~5 h, then annealed in high vacuum (~5 × 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 Cu Kα 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 (λ=0.1076 Å).

As confirmed by the XRD analysis, the samples thus obtained are of single phase with the cubic 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 ~11.468 to ~11.601 Å upon hydrogenating, with the rela-
thermomagnetic curves of LaFe$_{11.5}$Si$_{1.5}$ under different pressures measured under a field of 0.01 T implies that the detected volume expansion is caused by interstitial hydrogen and the ferromagnetic-paramagnetic 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 LaFe$_{11.5}$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 $-194$ to $-356$ K after hydrogenation, while progressively decreases with the release of hydrogen. In contrast, high pressure depresses $T_C$, and a $T_C$ drop of $-106$ 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 ($-296$ 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 $-296$ K, $\beta$ is the lattice expansion accompanying the FM-PM transition, and $\Delta a = 8.2 \times 10^{-6}$ K$^{-1}$ is the linear expansivity of LFS. $\Delta a$ 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 $-0.044$ Å, essentially independent of Si content.

As shown in Fig. 3 a linear increase of $T_C$ with $a$ at a rate of $-1510$ K/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 LaFe$_{11.5}$Si$_{1.5}$ was analyzed by synchrotron radiation XRD conducted under the pressures of up to 4.1 GPa. Thus, the compressibility obtained is $\kappa = -V^{-1}dV/dP = 8.639 \times 10^{-6}$ GPa$^{-1}$, where $P$ is pressure and $V$ is the vol-
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 La$_{1-x}$Ce$_x$Fe$_{11.5}$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 near 1510 K/Å but considerably larger under pressures ~2450 K/Å.

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 hydrogenation, 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 $H\Delta M/\Delta(S+\Delta S) \approx 4.2$ K, where $\Delta S$ and $\Delta M$ are the entropy and magnetization changes, respectively, as LaFe$_{11.5}$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 $\Delta T_C \approx 4.2(P\Delta V/H\Delta M) = 0.0739PV(\Delta M/MS)^2/H\Delta M$ ($H = 1$ T), based on the simple relation $\Delta V/V = 0.0176(\Delta M/MS)^2$, 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 $MS$ 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 ~11.416 and ~11.563 Å, corresponding to $P = 1$ GPa and $\delta = 2$, 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 ~1510 K/Å, 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 exists as a support to the crystal structure. A Rietveld analysis of the XRD data has been performed for the sample LaFe$_{11.5}$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 (Fe/Si)$_{11}$icosahedrons. There is a linear relation between bond length and lattice constant. The average Fe–Fe bond length increases from ~2.518 to ~2.539 Å when the lattice constant grows from ~11.468 to ~11.601 Å. It has been well established that the Fe–Fe interaction undergoes a monotonous increase with the Fe–Fe distance when the latter varies in the range from 2.45 to 2.6 Å. In this picture, the lattice expansion due to the incorporation of hydrogen will enhance the magnetic coupling between Fe atoms, thus, stabilize the PM phase. In fact, an increase in the dispersion coefficient of spin waves has been observed by Fujita and Fukamichi$^9$ 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 $T_C = (U_{PM} - U_{FM})/(S_{PM} - S_{FM})$ 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 $U_{PM}$, 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 $M^2$ 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 dominant 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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$^7$J. Shen, B. Gao, Y. X. Li, and B. G. Shen (unpublished).