Magnetic coupling between rare-earth and iron atoms in the La$_{1-x}$R$_x$Fe$_{11.5}$Si$_{1.5}$ (R=Ce, Pr, and Nd) intermetallics

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A systematic investigation on the effect of R doping, particularly the magnetic coupling between R and Fe, has been performed for the La$_{1-x}$R$_x$Fe$_{11.5}$Si$_{1.5}$ intermetallics (R=Ce, Pr, and Nd). A magnetic interaction comparable to that between Fe atoms is found between the R and Fe atoms, which causes an enhancement of the Curie temperature up to ~11% when ~30% of the La atoms are replaced by R. The R–Fe coupling is further found to be strongly dependent of the species of the rare earths. It monotonically grows as R sweeps from Ce to Nd. This could be a consequence of the lanthanide contraction, which causes an enhancement of the intra-atomic magnetic coupling. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2921781]

A key problem for the practical application of magnetic refrigeration is the discovery of effective refrigerants. Suitable refrigerants are expected to exhibit a considerably strong magnetocaloric effect (MCE). In the past decade, an intensive exploration for giant MCE materials has been stimulated by the discovery of Gd$_5$(Si,Ge)$_4$,[1] MnAs,[2] and La(Fe,Si)$_{13}$,[3] which exhibit extraordinarily strong MCE. Compared to the two former compounds, La(Fe,Si)$_{13}$ is especially attractive due to its promising magnetocaloric property, easy preparation, and low cost. A satisfactory performance has also been gained by a recent test for its capability of magnetic cooling.[4] However, from the viewpoint of practical application, it is still highly desired that the MCE of La(Fe,Si)$_{13}$ can be further improved. This is also the purpose of the continuous efforts since the discovery of this material in 2001.[3] It was recently found that the MCE of the compounds could be greatly modified by partially replacing La with magnetic rare earth atoms (R). For instance, the entropy change grows from ~29 to ~34 J/kg K, for a field change of 5 T, after 20% La were substituted by Ce in LaFe$_{11.7}$Si$_{1.3}$.[5] In the meantime, the Curie temperature T_C decreases from ~184 to ~173 K. A remarkable result is the depression of magnetic hysteresis by the incorporation of R. It has been reported that the magnetic hysteresis of La$_{0.3}$Pr$_{0.7}$Fe$_{11.18}$Si$_{1.82}$ is considerably smaller than that of LaFe$_{11.44}$Si$_{1.56}$, though the latter exhibits a higher T_C.[6] The distinctive properties of La$_{1-x}$R$_x$(Fe,Si)$_{13}$ are proposed to have a close relation with the magnetic interaction between R and Fe. We noted that despite the intensive work on R doping, a quantitative study on the R–Fe coupling is still lacking. This will no doubt impede the deep understanding of the magnetic properties of La$_{1-x}$R$_x$(Fe,Si)$_{13}$. In this letter, we performed a systematic investigation on the effect of R doping for the LaFe$_{11.5}$Si$_{1.5}$ intermetallics. Significant magnetic interaction, comparable to that between Fe atoms, is found between the R and Fe atoms. The R–Fe coupling displays a strong dependence on the species of the rare earths, and a monotonic increase is

observed as R sweeps from Ce to Pr and Nd.

Intermetallics with the nominal compositions of La$_{1-x}$R$_x$Fe$_{11.5}$Si$_{1.5}$ (R=Ce, Pr, and Nd and x=0–0.5) were prepared by arc-melting appropriate starting materials (99.9% or higher in purity) under a purified argon atmosphere and a following postannealing in high vacuum. The detailed procedures for the sample preparation can be found elsewhere.[3]

Powder x-ray diffraction (XRD) was performed at the ambient temperature by the Rigaku D/max-2400 diffractometer. It is found that the samples are nearly single phase with a cubic structure when x=0–0.3 for R=Ce and Nd, and x=0–0.5 for R=Pr. Figure 1 shows the typical XRD patterns of La$_{0.7}$Nd$_{0.3}$Fe$_{11.5}$Si$_{1.5}$. Similar XRD spectra are obtained for all of the samples, suggesting the similar structures of different samples. However, a close view of the XRD patterns shows a continuous, yet considerable, high-angle shift of the Bragg reflection of the samples La$_{0.7}$R$_{0.3}$Fe$_{11.5}$Si$_{1.5}$ as R sweeps from La to Pr, and Nd. This is a signature of lattice contraction due to the partial replacement of La by smaller rare earths. The maximal and minimal lattice constants are,
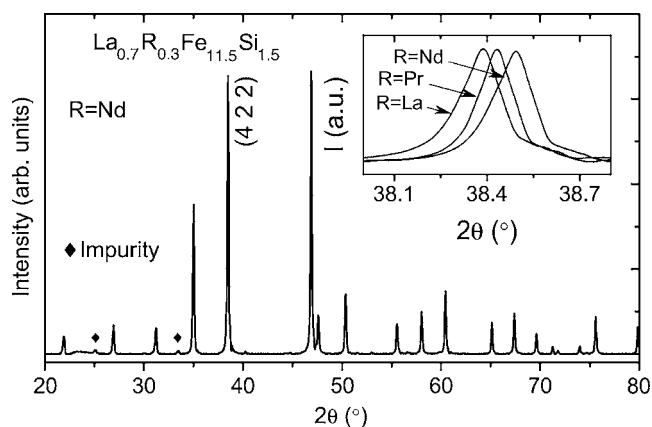

FIG. 1. Typical XRD patterns of La$_{0.7}$Nd$_{0.3}$Fe$_{11.5}$Si$_{1.5}$ collected at the ambient temperature. Diamonds show the presence of minor LaSi$_2$ phase. Inset plot: A close view that shows a high-angle shift of the (4 2 2) peak after the incorporation of R=Pr and Nd in La$_{0.7}$R$_{0.3}$Fe$_{11.5}$Si$_{1.5}$.

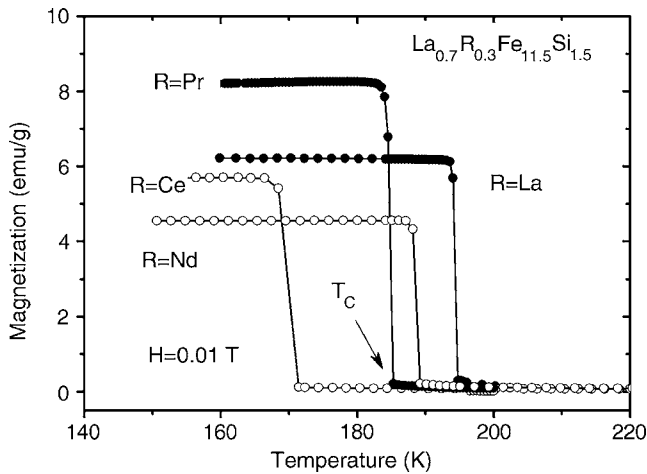a)Author to whom correspondence should be addressed. Electronic mail: jrsun@g203.iphyac.cn.

FIG. 2. Magnetization as a function of temperature for the $La_{0.7}R_{0.3}Fe_{11.5}Si_{1.5}$ compounds measured under a field of 0.01 T.

FIG. 3. (Color online) Phase volume dependence of the Curie temperature of $La_{0.7}R_{0.3}Fe_{11.5}Si_{1.5}$ (solid symbols). The T_C-V relation of the $LaFe_{13-x}Si_x$ compounds is also presented for comparison (open circles). Inset plot shows the $\Delta T_C/T_C-x$ relation, where ΔT_C is the difference of the Curie temperatures of the $La_{1-x}R_xFe_{11.5}Si_{1.5}$ and $LaFe_{11.5}Si_{1.5}$ compounds under the same phase volume. Solid lines are guides for the eye.

respectively, $\sim$11.468 Å obtained in $LaFe_{11.5}Si_{1.5}$ and $\sim$11.439 Å obtained in $La_{0.7}Nd_{0.3}Fe_{11.5}Si_{1.5}$.

Magnetic measurements were performed on a superconducting quantum interference device magnetometer. As a representative, Fig. 2 exemplifies the temperature-dependent magnetization (M) of $La_{0.7}R_{0.3}Fe_{11.5}Si_{1.5}$, obtained under a magnetic field of 0.01 T. The Curie temperatures, defined by the rigid corner of the M-T curves, are $\sim$194.1, $\sim$170.2, $\sim$184.9, and $\sim$189.0 K, corresponding to R=La, Ce, Pr, and Nd, respectively. As expected, obvious decreases of T_C occur after the partial substitution of R for La. A remarkable discovery of the present study is the strong dependence of the doping effects on the R species. Different from the lattice parameter, which displays a continuous contraction as R goes from La to Ce, Pr, and Nd, T_C decreases along the sequence from La to Nd, Pr, and Ce. The maximal Δa appears in $La_{0.7}Nd_{0.3}Fe_{11.5}Si_{1.5}$, whereas the maximal ΔT_C occurs in $La_{0.7}Ce_{0.3}Fe_{11.5}Si_{1.5}$. This feature remains for other R contents, and a simple analysis shows that T_C decreases with x at a rate of $\sim$20.8 K/atom for R=Nd, $\sim$32.3 K/atom for R=Pr, and $\sim$85.9 K/atom for R=Ce.

As a supplement, it should be pointed out that the external field of 0.01 T used for the magnetization measurements is far from the saturation field and is more representative of the initial magnetization. Since the demagnetization limit can depend on various aspects including sample geometry, the R dependence of the M values in the ferromagnetic state cannot be compared.

Although the doping effect of R varies from sample to sample, the generic tendency is clear, it yields a considerable depression of T_C. This result implies the presence of additional factors that affect the Curie temperature considering the fact that the R-T coupling is expected to have a positive contribution to T_C. As demonstrated by the data in Fig. 1, the incorporation of smaller R atoms leads to significant lattice shrinkage. This, according to our previous work, will cause a depression of the exchange integral between Fe atoms due to the reduction of Fe–Fe distances.[7] From the systematic investigation of the magnetic coupling under high pressures, which yield a lattice contraction without changing sample composition, it has been found that the decrease of phase volume leads to a T_C reduction at a rate of $\sim$3.72 K/Å^3 (marked by solid circles in Fig. 3). The Curie temperatures of the $LaFe_{13-x}Si_x$ compounds, with the Si content varying be-

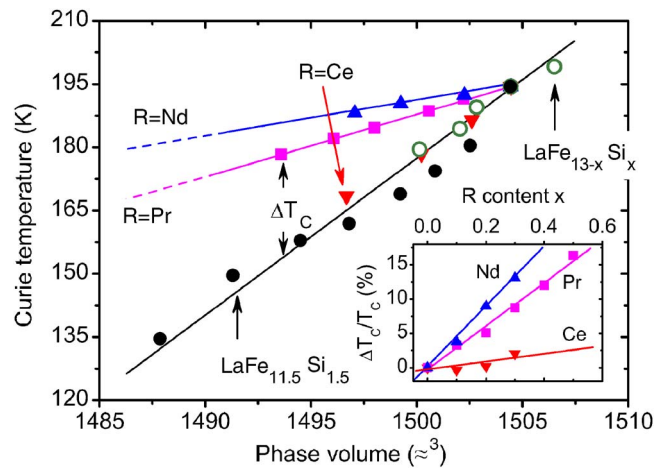tween 1.3 and 1.9, are also presented in Fig. 3 for comparison (open circles). A similar T_C-V relation to that of the $LaFe_{11.5}Si_{1.5}$ compound under pressures is obtained if only the lattice effects caused by the Si-doping are considered.[8] These results indicate the universality of the T_C-V ($V=a^3$) relation for the samples with only the Fe–Fe interaction. It can be clearly seen that the incorporation of R results in a significant change of the T_C-V relation (solid squares and triangles in Fig. 3). Although T_C linearly diminishes with the decrease of lattice constant (i.e., the increase of R content), the decrease rate is less rapid compared with that of $LaFe_{11.5}Si_{1.5}$. This feature becomes increasingly obvious as R goes from Ce to Nd, and a simple calculation gives the T_C-V slopes of $\sim$0.85, $\sim$1.47, and $\sim$3.52 K/Å^3, respectively, for the Nd-, Pr-, and Ce-doped compounds. All of these values are smaller than that of $LaFe_{11.5}Si_{1.5}$ ($\sim$3.72 K/Å^3) to different extents.

For a further analysis, the deviations of the T_C-V relations of $La_{1-x}R_xFe_{11.5}Si_{1.5}$ from that of $LaFe_{11.5}Si_{1.5}$, defined as $\Delta T_C/T_C=[T_C(R)-T_C(La)]/T_C(La)$, are presented in the inset plot of Fig. 3, where $T_C(R)$ and $T_C(La)$ are the Curie temperatures of the $La_{1-x}R_xFe_{11.5}Si_{1.5}$ and $LaFe_{11.5}Si_{1.5}$ compounds, respectively, with the same phase volume. $\Delta T_C/T_C$ shows a linear increase with the content of R, at the rate of $\sim$44.4 for $La_{1-x}Nd_xFe_{11.5}Si_{1.5}$, $\sim$31.9 for $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$, and $\sim$6.7 for $La_{1-x}Ce_xFe_{11.5}Si_{1.5}$. The typical value of $\Delta T_C/T_C$ is $\sim$15%, occurring in the Nd- and Pr-doped compounds with the R content of $\sim$0.3. The utmost values, obtained by extrapolating the $\Delta T_C/T_C$-x relation to $x=1$, of $\Delta T_C/T_C$ would be $\sim$43% and $\sim$31% for the fictitious compounds of $NdFe_{11.5}Si_{1.5}$ and $PrFe_{11.5}Si_{1.5}$, respectively.

As is well known, the Curie temperature of the rare-earth-transition-metal compound is jointly determined by the T-T, R-T, and R-R interactions (T is for transition metal). In general, the T-T interaction is the strongest, while the R-R exchange is the weakest. The Curie temperature of $LaFe_{13-x}Si_x$ should be exclusively determined by the Fe–Fe interaction because of the nonmagnetic character of La. However, the incorporation of magnetic R could introduce a coupling between R and Fe, which causes a difference of the

Curie temperatures of $La_{1-x}R_xFe_{11.5}Si_{1.5}$ and $LaFe_{11.5}Si_{1.5}$ (the Fe–Fe coupling in both compounds should be the same when phase volumes are similar).[9]

As will be seen below, T_C can be an appropriate measure of the magnetic coupling. According to the standard thermodynamics theory, the free energy of the ferromagnetic (FM) state will be equal to that of the paramagnetic (PM) state at T_C for a first-order phase transition. A direct derivation 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. It is easy to obtain

$$\Delta T_C \approx \frac{T_C(La)[\Delta S(La) - \Delta S(R)] + U_{FM}(La) - U_{FM}(R)}{\Delta S(R)}, \quad (1)$$

where $\Delta S(R)$ and $U(R)$ are the isothermal entropy change and the internal energy of the R-doped compounds, respectively. The approximation equality $U_{PM}(La) \approx U_{PM}(R)$ (because of the similarity of phase volumes) has been adopted for the derivation of Eq. (1). A direct calculation shows that the contribution of the first term of Eq. (1) is negligibly smaller compared with the observed ΔT_C. This implies that the variation of T_C is mainly due to the decrease of the internal energy from $U_{FM}(La)$ to $U_{FM}(R)$. Noting the fact that the only difference of $La_{1-x}R_xFe_{11.5}Si_{1.5}$ and $LaFe_{11.5}Si_{1.5}$ is the presence of magnetic R in the former, it is therefore plausible to ascribe the reduction of $U_{FM}(R)$ to the $R-T$ exchange. This means that ΔT_C can be a proper quantification for the $R-T$ coupling.

It is interesting to note that the $R-T$ interaction shows a strong dependence on the R species. The nearly coincidence of the $T_C - V$ curve of $La_{1-x}Ce_xFe_{11.5}Si_{1.5}$ with that of $LaFe_{11.5}Si_{1.5}$ indicates that the $R-T$ interaction between La and Ce is rather weak. The $R-T$ coupling is continuously enhanced as R goes from Ce to Pr and Nd, as demonstrated by the increase of the $T_C - V$ slopes. This is a feature similar to that observed in other rare-earth-transition-metal compounds. It could be ascribed to the lanthanide contraction, which causes an increase of the intra-atomic coupling between the $4f$ and outside electrons of R.[10]

It would be instructive to compare the $R-$Fe coupling in $La_{1-x}R_xFe_{11.5}Si_{1.5}$ with that in the typical rare-earth-transition-metal compound $R_2Fe_{14}B$. Take $Gd_2Fe_{14}B$ as an example. It has been reported that for this compound J_{R-T} and J_{T-T}, which are the parameters describing the $R-T$ and $T-T$ interactions, are -1.6×10^{-22} and 4.7×10^{-22} J, respectively. This means that the magnetic coupling between the R and Fe atoms is about one third of that between Fe atoms ($J_{RFe}/J_{FeFe} = 0.34$). A simple calculation further shows $\Delta T_C/T_C = [T_C(Gd_2Fe_{14}B) - T_C(La_2Fe_{14}B)]/T_C(Gd_2Fe_{14}B) \approx 21.8\%$, supposing the equivalence of the Fe–Fe couplings in $La_2Fe_{14}B$ and $Gd_2Fe_{14}B$.[11] It is a value in good agreement with that obtained for the $La_{1-x}R_xFe_{11.5}Si_{1.5}$, though the crystal structures of these two kinds of compounds are somewhat different. This result suggests the similarity of the mechanisms for the $R-T$ interaction in $La_{1-x}R_xFe_{11.5}Si_{1.5}$ and $R_2Fe_{14}B$.

In summary, a systematic investigation on the effect of R doping, particularly the magnetic coupling between R and Fe, has been performed for the $La_{1-x}R_xFe_{11.5}Si_{1.5}$ intermetallics (R=Ce, Pr, and Nd). Significant magnetic interaction, comparable to that between Fe atoms, is found between the R and Fe atoms, which causes a relative variation of the Curie temperature of $\sim 15\%$ even when only $\sim 30\%$ of the La atoms are replaced by R. The $R-$Fe coupling displays a strong dependence on the species of the rare earths. It is the weakest between Ce and Fe, and monotonically grows as R goes from Ce to Pr and Nd. This could be a consequence of the shrinkage of La series, which causes an enhancement of intra-atomic magnetic coupling.

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[8] A T_C-x relation can be first obtained for the compounds $LaFe_{13-x}Si_x$. Furthermore, a different T_C-x relation without volume change can be deduced following the procedure depicted in Ref. 7. The difference of the two sets of Curie temperatures $\Delta T_C(x) = T_C(x) - T_C(x)$ describes the effect merely due to the change of phase volume.

[9] It has been experimentally proved that the Fe–Fe distances are the same for different $LaFe_{13-x}Si_x$ compounds with a similar phase volume.

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