Hyperfine interactions and band structures of LaFe\textsubscript{13-\(x\)}Si\(_x\) intermetallic compounds with large magnetic entropy changes

Guang-jun Wang, Fang Wang, Nai-li Di, Bao-gen Shen, Zhao-hua Cheng*

State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

Received 4 August 2005; received in revised form 3 October 2005

Available online 18 November 2005

Abstract

Magnetic properties and hyperfine interactions of LaFe\textsubscript{13-\(x\)}Si\(_x\) intermetallic compounds with large magnetic entropy changes were investigated by means of Mössbauer spectroscopy, band structure calculation and magnetization measurements. It was found that the \(^{57}\text{Fe}\) magnetic hyperfine field at Fe\(_I\) (8b) site is larger than that at the Fe\(_II\) (96i) site, whereas the magnetic moment of Fe atoms at the Fe\(_I\) site is smaller than that of Fe atoms at the Fe\(_II\) site. The temperature dependence of the average \(^{57}\text{Fe}\) magnetic hyperfine field was found to deviate from the mean field model close to \(T_C\), implying that the first-order magnetic phase transition is predominant in the sample of LaFe\(_{11.7}\)Si\(_{1.3}\), and consequently results in a large magnetic entropy change. Furthermore, the effect of Si substitution for Fe on hyperfine parameters was investigated.

\(\text{PACS: } 75.30.Sg; 75.50.Bb; 76.80+y\)

Keywords: Magnetic entropy; Mössbauer spectroscopy; Band structure

1. Introduction

The discovery of a giant or large magnetocaloric effect in Gd\(_2\)Si\(_2\)Ge\(_2\) \[1\], MnFe\(_{1-x}\)As\(_x\) \[2\] and La(Fe\(_{1-x}\)Si\(_x\))\(_{13}\) intermetallic compounds \[3–6\] has given rise to interest in searching for materials with a first-order magnetic phase transition for use as magnetic refrigerants. Among them, the La(Fe\(_{1-x}\)Si\(_x\))\(_{13}\) intermetallic compounds with a low Si content undergo an itinerant-electron metamagnetic transition above the Curie temperature \(T_C\) and a first-order magnetic phase transition at \(T_C\), which result in a large magnetic entropy change \[3–6\]. In our previous work, applied field Mössbauer spectroscopy was performed to understand the connection between field-induced magnetic phase transition and magnetic entropy change above \(T_C\) from a microscopic point of view \[7,8\]. In the LaFe\(_{13-\(x\)}\)Si\(_x\) intermetallic compounds, Fe atoms occupy two non-equivalent sites, 8b(Fe\(_I\)) and 96i(Fe\(_II\)), respectively. La and Fe\(_I\) atoms form a CsCl structure. The Fe\(_I\) atoms are surrounded by an icosahedron of twelve Fe\(_II\) atoms, while the Fe\(_II\) atoms have 1 Fe\(_I\) atom and 9 Fe\(_II\) atoms as the nearest neighbors \[9\]. Since the previous reports focused only on the magnetic-field-induced phase transition above \(T_C\), rather than the hyperfine interactions at these two non-equivalent sites, we fitted the ferromagnetic phase with one sextet and the paramagnetic phase with a doublet by using average hyperfine parameters. The detailed information regarding the effect of Si substitution for Fe on the hyperfine interactions at these two non-equivalent Fe sites is not yet well understood.

In LaFe\(_{13-\(x\)}\)Si\(_x\) compounds, the substitution of Si for Fe produces two effects, i.e. the lattice contraction and the hybridization between the electronic orbitals of Si and Fe atoms. In order to investigate the effect of the hybridization between the electronic orbitals of Si and Fe atoms on the magnetic properties and hyperfine interactions at Fe\(_I\) and Fe\(_II\) sites, respectively, a combined \(^{57}\text{Fe}\) Mössbauer spectroscopy and band structure calculation was carried out.
2. Experiments and band calculation

LaFe$_{13-x}$Si$_x$ compounds were prepared by arc melting in an atmosphere of highly pure argon gas. The purity of the starting elements was better than 99.9 wt%. The ingots were remelted three times to ensure homogeneity, annealed in vacuum at 1273 K for 50 days and then quenched in liquid nitrogen. All magnetization measurements were performed using a superconducting quantum interference device (SQUID) magnetometer. Mössbauer spectra of LaFe$_{13-x}$Si$_x$ (x = 1.3, 1.7, and 2.0) were measured at temperatures ranging from 20 to 300 K, which were acquired by a constant acceleration Mössbauer spectrometer using a $^{57}$Co source diluted in a rhodium matrix. The velocity was calibrated using an α-Fe foil. The values of the center shift (CS) are relative to α-Fe at room temperature. For ideal absorber thickness, the mass of absorber material used was 16 mg/cm$^2$.

The self-consistent full-potential linearized augmented-plane-wave (FP-LAPW) method with the generalized gradient approximation was employed to calculate the band structures and consequently, the magnetic moments and hyperfine parameters. Si atoms were observed to occupy mainly the FeII site in LaFe$_{13-x}$Si$_x$ compounds [9]. In order to simulate the homogenous distribution of Si atoms at the 96i(FeII) site and to avoid the supercell containing too many atoms for calculation, we used a cell that included 8 La atoms at the 8a site, 8 Fe atoms at the 8b(FeI) site, and 84 Fe atoms together with 12 Si atoms at the 96i(FeII) site. Therefore the composition of the calculated compound is LaFe$_{11.5}$Si$_{1.5}$. For comparison, the LaFe$_{13}$ hypothetical compound was also selected for calculation. The Brillouin-zone sampling was performed using 56 special k points for x = 0 and eleven special k points for x = 1.5 in the irreducible Brillouin zone. Throughout the present calculations, we ensured the total energy and the charge convergence.

3. Results and discussions

Fig. 1 illustrates $^{57}$Fe Mössbauer spectra of LaFe$_{13-x}$Si$_x$ compounds with x = 1.3, 1.7, and 2.0 collected at 20 K. The Mössbauer spectra were fitted with a least-squares method program assuming Lorentzian peaks. This fitting model assumes that the hyperfine interactions are effectively static and the observed lines shapes can be modeled as several Lorentzian singlets, doublets or sextets, corresponding to paramagnetic sites with or without a quadrupole splitting and magnetic sites with a magnetic hyperfine field and a quadrupole shift. For magnetic sites, the magnetic hyperfine field produces the dominant interaction. The first-order perturbation result was used. The required parameters are limited to the CS the magnetic hyperfine field, $H_{hf}$, the quadrupole shift $\varepsilon$, and the angle between the incident γ-ray and $H_{hf}$, $\theta_{hf}$. Since there are two non-equivalent Fe sites, FeI and FeII, and Si atoms mainly occupy the FeII sites site in LaFe$_{13-x}$Si$_x$ compounds [9], all spectra of the ferromagnetic phases were fitted by using two sextets for the FeI and FeII sites with an absorption area ratio of about 1:12–x. For the FeI sextet, the line widths were set equal to one another. For the FeII sextet, due to the broad distribution of $H_{hf}$ at the FeII site originating from Si atoms, we use a sextet with the broadened lines to fit the FeII site in order to reduce the fitting parameters. The magnetic hyperfine fields given here for the FeII site are average ones. Therefore, the line widths are not equal and the relative amplitudes deviate significantly from 3:2:1:1:2:3. However, the relative absorption areas for the six peaks are maintained to be 3:2:1:1:2:3 owing to the isotropic orientation to the γ-ray direction of the magnetic grains.

It is well known that a rough formula $H_{hf} = A\mu_F$ is usually used to elucidate the relationship between the magnetic hyperfine field, $H_{hf}$, and the magnetic moment, $\mu_F$ [10]. However, the situation is more complex for both Fe sites in the LaFe$_{13-x}$Si$_x$ compounds. Although the $^{57}$Fe magnetic hyperfine field at FeI site is larger than that at the FeII site, neutron diffraction results demonstrate that the magnetic moment of Fe atoms at FeII site is smaller than that at FeII site [9]. In order to understand the relationship between the local magnetic moment of Fe atoms and $^{57}$Fe
magnetic hyperfine fields, the partial density of states (DOSSs) for FeI and FeII sites of LaFe13 and LaFe11.5Si1.5 (Fig. 2) was calculated by the spin-polarized band structure calculations. Magnetic moments of Fe atoms at these two non-equivalent sites are obtained by counting the number of electrons occupying the majority and minority sub-bands. The calculated magnetic moments (Table 1) were 1.74 and 2.22 $\mu_B$ at FeI and FeII sites for LaFe11.5Si1.5, which were comparable with the refinement values of 1.54 and 2.16 $\mu_B$ at FeI and FeII sites for LaFe11.6Si1.6 by means of neutron diffraction [9]. It was well known that the Fe–Fe exchange interaction is strongly dependent upon the Fe–Fe interatomic distance. According to Givord and Lemaire [11], there are two kinds of Fe–Fe exchange interactions, a positive and a negative one, depending on the Fe–Fe interatomic distance. When the separation of the Fe–Fe pair is smaller than 2.45 Å the exchange interaction is negative while the interaction is positive at a larger Fe–Fe distance. A weaker FeI–FeII overall exchange interaction is expected since the FeI–FeII (≈2.45 Å) interatomic distance is shorter than that of FeII–FeII (≈2.56 Å) [9]. This expectation was supported by the fact of the enhancement of Curie temperature with increasing Fe–Fe interatomic distance in LaFe13–Si$_x$ compounds [12]. Therefore, the exchange splitting of density of states between the majority and minority sub-bands at the Fermi level for FeI site is

\[
E_{\text{hf}}^{\text{FeI}} = E_{\text{hf}}^{\text{FeII}} + \Delta E_{\text{hf}}
\]

where $E_{\text{hf}}^{\text{FeI}}$ and $E_{\text{hf}}^{\text{FeII}}$ are the hyperfine field constant at FeI and FeII sites, respectively. The difference between the hyperfine field constants at these two sites arises mainly from the influence of different Fe–Fe interatomic distances on the s–d exchange polarization of the conduction electrons. Shorter FeI–FeII interatomic distances and larger number of nearest neighbors of Fe atoms produce a larger THF at the FeI site.

Based on the evaluation of Stearns [14], the hyperfine field constant $A$ in $\alpha$-Fe reaches 90 kOe/$\mu_B$. From solution of the simultaneous equations of Eq. (4) for each site with the calculated magnetic moments, the transferred hyperfine coupling constants at FeI and FeII sites are $C_I = 6.2$ kOe/$\mu_B$ and $C_{II} = 5.2$ kOe/$\mu_B$, respectively. The difference between the hyperfine field constants at these two sites arises mainly from the influence of different Fe–Fe interatomic distances on the s–d exchange polarization of the conduction electrons. Shorter FeI–FeII interatomic distances and larger number of nearest neighbors of Fe atoms produce a larger THF at the FeI site.

Fig. 3 illustrates the DOSs of Fe-s, Fe-d and Si-sp orbitals for the LaFe13 hypothetical compound and the LaFe11.5Si1.5 compound. The DOSs of the Fe-3d down spin states consists of two prominent peaks and the Fermi energy is pinned at the deep valley between them, which reflects that this electronic system is stabilized with the help of spin polarization. This distinctive feature was also found in the Y(Fe11Ti) compound by Li and Coey [17]. With

![Fig. 2. Partial density of states (DOSSs) for FeI and FeII sites of LaFe13 and LaFe11.5Si1.5.](image-url)
increasing Si content, the volume of the unit cell decreases and the Fermi level shifts to higher energy. The DOSs distribution of spin-up states and spin-down states of Fe-d orbital shifts towards higher and lower energy, respectively.

Fig. 4 shows the temperature dependence of the average hyperfine field for the compounds LaFe$_{13-x}$Si$_x$ with $x = 1.3$, 1.7, and 2.0. In order to compare the experimental values of magnetic moments and hyperfine fields with the magnetic moments and hyperfine fields at 0 K calculated via band structure, the hyperfine field in the ground state $H_{hf}(0)$ can be derived by fitting the curves that were fitted with Brillouin function (BF) according to the equation

$$H_{hf}(T) = H_{hf}(0)B_{1/2}(h_{hf}(T)/t),$$

where $B_{1/2}(x) = 2 \coth(x) - \coth(x)$ is the BF, and $t = T / T_C^{BF}$. $T_C^{BF}$ is the temperature of $H_{hf}(T_C) = 0$ obtained from the mean field model.

The extrapolated values of magnetic hyperfine fields for Fe$_I$ and Fe$_{II}$ sites at 0 K are summarized in Table 1, which are in good agreement with those calculated via band structure calculations at 0 K.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$H_{hf}(Fe_I)$ (kOe)</th>
<th>$H_{hf}(Fe_{II})$ (kOe)</th>
<th>$\mu_{Fe}(Fe_I)$ ($\mu_B$)</th>
<th>$\mu_{Fe}(Fe_{II})$ ($\mu_B$)</th>
<th>$\Delta(Fe_I)$ (mm/s)</th>
<th>$\Delta(Fe_{II})$ (mm/s)</th>
<th>IS (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>369</td>
<td>339</td>
<td>2.13</td>
<td>2.40</td>
<td>0.000</td>
<td>0.464</td>
<td>0.15</td>
</tr>
<tr>
<td>1.3</td>
<td>326(3)</td>
<td>296(2)</td>
<td>2.13</td>
<td>2.40</td>
<td>0.000</td>
<td>0.468(13)</td>
<td>0.19(2)</td>
</tr>
<tr>
<td>1.5</td>
<td>313</td>
<td>291</td>
<td>1.74</td>
<td>2.22</td>
<td>0.117</td>
<td>0.317</td>
<td>0.20</td>
</tr>
<tr>
<td>1.7</td>
<td>312(3)</td>
<td>281(2)</td>
<td>1.54</td>
<td>2.16</td>
<td>0.000</td>
<td>0.474(13)</td>
<td>0.21(2)</td>
</tr>
<tr>
<td>2.0</td>
<td>294(3)</td>
<td>261(2)</td>
<td>0.000</td>
<td>0.482(11)</td>
<td>0.22(2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. Density of states of Fe-s, Fe-d and Si-sp orbitals for LaFe$_{13}$ and LaFe$_{11.5}$Si$_{1.5}$ compounds.

Fig. 4. Temperature dependence of the average hyperfine field for LaFe$_{13-x}$Si$_x$ compounds.
Although the curves can be well fitted at low temperatures, the BF relation fails to fit the $H_{hf}(T)$ close to the $T_C$. As the mean field theory presumes the magnetic transition at $T_C$ to be of second order, in the LaFe$_{11.7}$Si$_{1.3}$ compound, the significant deviation of the BF relation from the temperature dependence of $H_{hf}(T)$ close to $T_C$ suggests that the magnetic phase transition is of a first-order nature. With increasing Si concentration, the second-order magnetic transition is predominant and leads to a larger magnetic entropy change. A similar temperature dependence of hyperfine fields of LaFe$_{13-x}$Si$_x$ in a narrow temperature range was also reported by Liu et al. [12]. On the basis of band structure and experimental results, the Si-dependence of hyperfine fields of LaFe$_{13-x}$Si$_x$ compounds are illustrated in Figs. 5(a) and (b), respectively. It can be noted that the calculated values are in good agreement with those obtained from magnetization measurements and Mössbauer measurements. As only the nearest-neighbor (nn) atoms are taken into account, the hyperfine field $H(m)$ at a given Fe site is assumed to be $H_{hf}(m) = H_{hf}(0) - m\Delta H_{hf}$, where $m$ is the number of the nearest neighbors occupied by Si atoms. $H_{hf}(0)$ is the hyperfine field at the Fe site without Si atoms as the nearest neighbors. $\Delta H_{hf}$ is the decrement in the hyperfine field as a result of replacing one Fe atom by one Si atom and is about 36.6 kOe.

In the case of ferromagnetic materials, the electric quadrupole interaction, i.e. the interaction of the nuclear quadrupole moment with the non-spherical part of the crystalline electrostatic potential [18,19], is a perturbation term in comparison with the magnetic hyperfine interaction. If the quadrupole interaction is much weaker than the magnetic hyperfine interaction, the quadrupole shift $\varepsilon$ can be written as [20]

$$\varepsilon = \frac{e^2 Q}{8} [2 - (3 - \eta \cos 2\phi_{hf}) \sin^2 \theta_{hf}],$$  

(6)

where $Q$ is the electric quadrupole moment of the $^{57}$Fe nucleus, Mössbauer parameters $\theta_{hf}$ and $\phi_{hf}$ are the polar and azimuthal angles defining the orientation of $H_{hf}$ relative to the principal axes ($x$, $y$, and $z$) of the electric field gradient (EFG) tensors $V_{ij}$ ($V_{ij} = \partial^2 V/\partial x^2$, $i,j = x,y,z$), and $\eta = (V_{xx} - V_{yy})/V_{zz}$ is the asymmetry parameter of the EFG tensors. $e = V_{zz}$ is the principal component of the EFG at the nucleus.

Since the quadrupole shift is much smaller than the magnetic Zeeman splitting in the case of ferromagnetic materials and the alignment of magnetic hyperfine field of polycrystalline sample with respect to the crystallographic axes was not known, it is difficult to determine precisely the on-diagonal quadrupole interaction. However, in the case of paramagnetic materials, when the hyperfine magnetic is nil, or effectively nil, the spectrum is either a singlet or a doublet. The quadrupole splitting, $\Delta$, can be written as [20]

$$\Delta = \frac{e Q V_{zz}}{2} \left(1 + \frac{\eta}{3}\right)^{1/2}.$$

(7)

Mössbauer spectra collected at $T > T_C$ provide the possibility to determine quadrupole splitting precisely. Fig. 6 displays the room-temperature Mössbauer spectra for LaFe$_{13-x}$Si$_x$ with $x = 1.3$, 1.7, and 2.0. The paramagnetic phase can be best fitted with one singlet and one doublet with an absorption area ratio of about 1:12, which are assigned to be contributions from Fe$_I$ and Fe$_{II}$ sites, respectively. The line widths of the singlet and doublet are about 0.13 and 0.18 mm/s, respectively. The fitted values of quadrupole splitting at these two non-equivalent sites $\Delta$(Fe$_I$) and $\Delta$(Fe$_{II}$) are also listed in Table 1.

On the basis of band calculation, the $V_{xx}$, $V_{yy}$, $V_{zz}$, and $\eta$ can be calculated from the total charge density. By using $Q = 0.16$ a.u. for the $^{57}$Fe nucleus [21], the values of quadrupole splitting at Fe$_I$ and Fe$_{II}$ sites, $\Delta$(Fe$_I$) and $\Delta$(Fe$_{II}$), are calculated for the compounds LaFe$_{13}$ and LaFe$_{13-x}$Si$_x$ and listed in Table 1.

Since the EFG is directly related to the asphericity of the electron density in the vicinity of the probe nucleus, the quadrupole splitting depends on the symmetry of the surrounding environment of the Fe atom. For the hypothetical compound LaFe$_{13}$, the quadrupole splitting at the Fe$_I$ site is zero owing to its highly symmetrical

![Fig. 5. Si-dependence of average magnetic moments and magnetic hyperfine fields for LaFe$_{13-x}$Si$_x$ compounds. For compounds with $x = 0$ and 1.5, the hyperfine fields were obtained from theoretical calculation. The average magnetic moment for $x = 1.6$ obtained from Ref. [9] was also plotted in Fig. 4(a) as an open square.](attachment:image-url)
environment of icosahedra formed by 12 FeII atoms. The FeI site symmetry is cubic m3 so that the electric field gradient disappears. The FeII site symmetry is monoclinic m so that there is a non-zero electric field gradient. The calculated values are consistent with the experimental values for $x = \frac{1}{3}, \frac{1}{7}, \frac{2}{3}$. The substitution of Si for Fe disturbs the highly symmetrical environment around FeI atom and results in quadrupole splitting. However, for the sample with $x = \frac{1}{5}$, the calculated quadrupole splitting at the FeI site of about 0.117 mm/s cannot be distinguished by Mössbauer spectra since it is smaller than the line width of the absorption peak for $\alpha$-Fe (about 0.130 mm/s). The theoretical value of $A(FeI)$ was found to be slightly smaller than the experimental one. This result suggests that the supercell includes 8 La atoms at the 8a site, 8 Fe atoms at the 8b(FeI) site, and 84 Fe atoms together with 12 Si atoms at the 96i(FeII) site are not large enough to simulate the real structure of LaFe$_{11.5}$Si$_{1.5}$ for calculating the electric field gradient at the $^{57}$Fe nuclei. On the other hand, since the magnetic moment is determined by the exchange splitting of density of states between the majority and minority sub-bands at the Fermi level, which is strongly dependent upon the numbers of the nearest-neighboring atoms and their interatomic distance, the supercell used in the present work is large enough for calculating the magnetic moments.

The Debye model gives the following expression for the recoil-free fraction [20]:

$$f = \exp \left[ -\frac{3E_R}{2k_B\Theta} \left( 1 + \frac{4T^2}{\Theta^2} \int_0^{\Theta/T} \frac{x}{e^x - 1} dx \right) \right]. \quad (8)$$

where $E_R$ is the recoil energy of Fe for the 14.4 keV $\gamma$-ray, and $\Theta$ represents Debye temperature, which can be obtained on the basis of the temperature dependence of the recoil-free fraction $f$. Since the source was at the same temperature during the measurements, the ratio of the recoil-free factor is equal to the ratio of the time-normalized resonant absorption spectral areas if the absorber is sufficiently thin. Therefore, the temperature dependence of time-normalized resonant absorption spectral areas can also be described in terms of the Debye model.

$$A \propto \exp \left[ -\frac{3E_R}{2k_B\Theta} \left( 1 + \frac{4T^2}{\Theta^2} \int_0^{\Theta/T} \frac{x}{e^x - 1} dx \right) \right]. \quad (9)$$

Fig. 7 shows the temperature dependence of the time-normalized resonant absorption spectral areas for the compounds with $x = 1.3, 1.7, \text{and} 2.0$. Solid lines indicate fitting results according to the Debye model.
compounds with $x = 1.3, 1.7,$ and 2.0. The Debye temperatures are calculated to be 317, 330 and 336 K for the compounds $x = 1.3, 1.7,$ and 2.0, respectively, by using the least-squares method from the temperature dependence of the time-normalized resonant absorption spectral areas below the Curie temperature. The Debye temperatures are in agreement with the results obtained by specific heat measurements [22].

The center shift (CS) obtained from Mössbauer spectra originates from the sum of isomer shift (IS) and the second-order Doppler shift (SOD).

$$CS(T) = IS + SOD(T).$$

(10)

Within the framework of the Debye model, the second-order Doppler shift can be calculated as

$$SOD(mm/s) = -\frac{3kT_D}{2Mc} \left[ \frac{3}{8} + 3 \left( \frac{T}{T_D} \right)^4 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} \right].$$

(11)

Thus, the temperature dependence of center shift can be written as

$$CS(T) = IS - \frac{3kT_D}{2Mc} \left[ \frac{3}{8} + 3 \left( \frac{T}{T_D} \right)^4 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} \right].$$

(12)

By fitting the experimental values of $CS(T)$ with the Debye model, the isomer shift can be obtained for the compounds with $x = 1.3, 1.7,$ and 2.0 according to Eq. (12).

It was known that isomer shift is directly related to the local charge density $\rho(0)$ at the nuclear position and provides unique information about charge-density changes on alloy formation [20]. For the compounds with $x = 0$ and 1.5, the isomer shift can be calculated from the total electron density at the nuclear site using $IS = \rho(0) - \rho_a(0)$, where we take $x$ as $-0.24$ mm/s [23].

Fig. 8 displays both average values of IS as a function of Si content. According to the calculation of Akai et al. [23,24], the isomer shifts in Fe alloys are essentially determined by the number of s-electrons of the Fe atom and the form of the s-wave functions is not very important. With increasing Si content, the hybridization of Si-p orbitals with Fe-d orbitals becomes stronger. On the other hand, both the intratomic and the interatomic hybridizations between the Fe-d states and Fe-s states decrease so that the Fe-s charge on the Fe site decreases. Therefore, the introduction of Si leads to an increase in isomer shift.

The temperature dependence of center shifts of La-Fe$_{13-x}$Si$_x$ compounds, as illustrated in Fig. 9, was also employed to identify the first-order magnetic phase transition in the sample of LaFe$_{11.7}$Si$_{1.3}$ since it is usually associated with a first-order crystallographic phase transition. Due to the second-order Doppler shift as mentioned above, the center shift was expected to decrease with increasing temperature. According to the Debye model, the temperature dependence of the center shift was also plotted in Fig. 9 for comparison. An abrupt drop in center shift was observed at $T_C$ for LaFe$_{11.7}$Si$_{1.3}$, accompanied by a sharp decrease of lattice constant as detected by neutron
diffraction during the first-order magnetic phase transition [9]. With increasing Si concentration, the drop of center shifts around \(T_C\) becomes less abrupt since the second-order magnetic phase transition is predominant in the samples with higher Si contents. For the sample with \(x = 2.0\), no obviously abrupt drop in the center shift was observed and the center shift as a function of temperature can be well fitted by Eq. (12).

4. Conclusions

Both band calculation and Mössbauer spectra demonstrated that the \(^{57}\)Fe magnetic hyperfine field at the Fe\(_I\) site is larger than that at the Fe\(_II\) site, whereas the magnetic moment of Fe atoms at the Fe\(_{II}(8b)\) site is smaller than that of Fe atoms at the Fe\(_{II}(96i)\) site. The temperature dependence of the average \(^{57}\)Fe magnetic hyperfine field and the average center shift was found to deviate from the mean field model close to \(T_C\) and Debye model above \(T_C\), respectively. Sharp drops of average magnetic hyperfine field and center shift around \(T_C\) imply that the first-order magnetic phase transition is predominant in the sample of LaFe\(_{11.7}\)Si\(_{1.3}\) and, consequently, results in a large magnetic entropy change. Owing to the hybridization between the electronic orbitals of Si and Fe atoms, the hyperfine field decreases, while the isomer shift increases with increasing Si content.

Acknowledgments

This work was supported by the State Key Project of Fundamental Research, the National High Technology Development Program, and the National Natural Science Foundation of China. Z.H.C thanks the Alexander von Humboldt Foundation for the financial support and generous donation of some Mössbauer equipments.

References