Large magnetovolume effects and band structure of itinerant-electron metamagnetic La(FexSi1-x)13 compounds


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Large magnetovolume effects and band structure of itinerant-electron metamagnetic \( \text{La(Fe}_x\text{Si}_{1-x})_{13} \) compounds

A. Fujita* and K. Fukamichi

Department of Materials Science, Graduate School of Engineering, Tohoku University, Aoba-yama 02, Sendai 980-8579, Japan

J.-T. Wang† and Y. Kawazoe

Institute for Materials Research, Tohoku University, Katahira 2-1-1, Sendai, 980-8577, Japan

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Among Fe-based ferromagnets, \( \text{La(Fe}_x\text{Si}_{1-x})_{13} \) compounds are the first example realizing the itinerant-electron metamagnetic transition from the paramagnetic to the ferromagnetic state, accompanied by a marked magnetovolume effects. The effect of pressure on the Curie temperature is one order larger than that on the spontaneous magnetization in analogy with the results for Fe-Pt invar-type alloys. The large pressure coefficient of \( T_C \), \( d \ln T_C/dP \), is attributed to the renormalization effect caused by spin fluctuations for free energy. The metamagnetic transition and the marked magnetovolume effects in the present compounds are related to the characteristic \( 3d \) band structures in analogy with Fe-Pt alloys in both the ferromagnetic and paramagnetic states.

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I. INTRODUCTION

It is well known that several kinds of Fe-based alloys, such as Fe-Ni and Fe-Pt, show a significantly large magnetovolume effect.\(^1,2\) In these alloys, the temperature dependence of the spontaneous magnetostriction compensates the lattice expansion due to anharmonic atomic vibration around a certain concentration, resulting in almost zero thermal expansion, i.e., invar effect. The origin of such a large magnetovolume effect in these alloys was investigated during last few decades and is still discussed as one of the important phenomena related to itinerant-electron ferromagnetism.\(^3,4\)

Theoretical researches of itinerant-electron ferromagnetism have been a great help in promoting fundamental understandings of the large magnetovolume effect in the invar-type alloys.\(^5-11\) Recent first-principles calculations based on the fixed-spin moment method reveal that the large magnetovolume effect is closely related to the degeneracy of more than two magnetic states,\(^5-11\) which are accompanied by the first-order phase transition. According to the calculations, the transition from the magnetic ordered to disordered state is classified into mainly three types.\(^11\) Namely, type I is a conventional second-order transition, and type II is the first-order transition between the magnetic ordered and the disordered state. Type III involves intermediate ordered states in evolution from the ordered state in the ground state to the disordered state. It has been pointed out that the magnetic phase transition in Fe-Pt invar-type alloy lies close to type II and the first-order transition between the ferromagnetic (F) and the paramagnetic (P) state is expected from theoretical calculations.\(^5-11\) However, to our knowledge, no experimental evidence for such a transition at the Curie temperature \( T_C \) has been observed in conventional invar-type alloys mentioned above. A martensitic transformation in these alloys\(^1,2\) may hinder the first-order magnetic phase transition.

The magnetic first-order transition in the itinerant-electron ferromagnets was discussed by Wohlfarth and Rhodes\(^12\) and the magnetic-field-induced first-order transition from the paramagnetic (P) to the ferromagnetic (F) state is predicted from the Stoner model. The field-induced first-order P-F transition in itinerant-electron magnets, which is so-called itinerant-electron metamagnetic (IEM) transition, has been investigated theoretically\(^13-18\) and experimentally\(^19-35\) by taking spin fluctuations and magnetovolume effects into consideration. The experimental candidates of the IEM transition have been limited to Co-based Laves\(^19-26\) and pyrite\(^27,28\) compounds until recent reports on the IEM transition in \( \text{UCoAl} \)\(^29\) and \( \text{MnSi} \) under hydrostatic pressure.\(^30\) Among Fe-based compounds, the IEM transition defined above has never been observed until we found in \( \text{La(Fe}_x\text{Si}_{1-x})_{13} \) compounds,\(^31-35\) although the following magnetic order-order metamagnetic (MT) transitions have been reported for Fe-based intermetallic compounds such as the ferromagnetic-antiferromagnetic transition in \( \text{Hf}_{1-x}\text{Ta}_x\text{Fe}_2 \),\(^36\) \( \text{Sc}_{1-x}\text{Ti}_x\text{Fe}_2 \),\(^37\) \( \text{Ce(Fe}_x\text{Al}_{1-x})_2 \) (Ref. 38) and \( \text{La(Fe}_x\text{Al}_{1-x})_{13} \) (Refs. 39 and 40) compounds and the ferromagnetic-ferromagnetic transition in \( \text{Sc}_{1-x}\text{Ti}_x\text{Fe}_2 \) (0.5 \( \leq x \leq 0.7 \)) compounds.\(^31\) Very recently, the unique features of the IEM transition observed in Co-based Laves and pyrite compounds, \( \text{MnSi} \) and \( \text{La(Fe}_x\text{Si}_{1-x})_{13} \) compounds are theoretically weighed against that of the order-order MT’s.\(^18\) The present \( \text{La(Fe}_x\text{Si}_{1-x})_{13} \) compounds with 0.84 \( \leq x \leq 0.90 \) show the thermal-induced first-order P-F phase transition at \( T_C \) and the field-induced IEM transition above \( T_C \) is caused by applying magnetic field.\(^31-35\) These characteristics are consistent with the theoretical model of the IEM transition based on the Landau expansion including the influence of spin fluctuations.\(^14-18\) According to this theory, the fourth-order Landau coefficient, which is the mode-mode coupling coefficient of spin fluctuations, becomes negative in the itinerant-electron metamagnets, resulting in a large magnetovolume effect.\(^15,16\) It should be noted that the negative fourth-order Landau coefficient in Fe-Pt and Fe-Ni invar-type alloys is also obtained by the fixed spin moment calculations.\(^6,9,42,43\) Therefore it is expected that the electronic structures of the present compounds are very close to the condition for occurrence of the large magnetovolume ef-
fants related to the first-order magnetic transition discussed on Fe-Pt alloys. In the present study, the characteristics of the compound SmFe_1-xSi_x are discussed by using the calculated band structures and compared with those in Fe-Pt and Fe-Ni invar-type alloys.

II. EXPERIMENTS AND BAND CALCULATION

The La(Fe_1-xSi_x)_{13} compounds were prepared by arc melting in an Ar atmosphere. To homogenize these specimens, the heat treatment was made in a vacuum quartz tube at 1323 K for 10 days. The thermal-expansion measurement was carried out by a three-terminal capacitance method and the linear thermal-expansion coefficient was obtained by a numerical differentiation. The high-field magnetic susceptibility was measured with a superconducting quantum interference device magnetometer. The electronic heat-capacity coefficient was measured by a relaxation method.

The band calculations were carried out by means of the self-consistent full-potential linearized augmented-plane-wave method with the generalized gradient approximation. To simulate the random distribution of Si, a 2x2x2 supercell (including 8 atoms of La, 92 of Fe, and 12 of Si) based on NaZn_{13} unit cell was used with the lattice parameter of 1.1468 nm and 24 of symmetry operations. Therefore the concentration of the calculated compound corresponds to La(Fe_{0.885}Si_{0.115})_{13}. The radii of the muffin-tin spheres were set to 0.1482 nm for La, 0.1164 nm for Fe, and 0.1217 for Si, respectively. The Brillouin-zone sampling is performed using 4 special k points in the irreducible Brillouin zone for such a large supercell. Convergences of the total energy and the charge were carefully checked throughout the present calculations.

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the linear thermal-expansion coefficient α for La(Fe_{1-x}Si_{x})_{13} (x = 0.84, 0.86, and 0.88) compounds. The spontaneous magnetostriction \( \omega_m(T) \) is expressed by

\[
\omega_m(T) = \frac{3}{2} \int \alpha_m(T) dT = k C_{mv}(M(T)^2 + \xi(T)^2),
\]

where \( \alpha_m(T) \) is the magnetic contribution of the linear thermal-expansion coefficient at T, k and \( C_{mv} \) are the compressibility and the magnetovolume coupling, and \( M(T) \) and \( \xi(T) \) are the amplitudes of local magnetic moment and spin fluctuations, respectively. For the second-order transition, \( M(T) \) continuously decreases and \( \xi(T) \) gradually increases with temperature, and therefore the temperature dependence of \( \omega_m(T) \) shows no drastic change at \( T_C \). On the other hand, \( M(T) \) discontinuously disappears at \( T_C \) because of the first-order transition. With increasing Fe concentration x, the discontinuous change of magnetization at \( T_C \) takes place. Accordingly, a negative broad peak of the thermal-expansion coefficient \( \alpha \) around \( T_C \) for \( x = 0.84 \) is attributed to the spontaneous magnetostriction. The negative peak of \( \alpha \) for \( x = 0.86 \) becomes shaper, and eventually \( \alpha \) for \( x = 0.88 \) shows a divergent behavior at \( T_C \) due to the first-order transition. By x-ray diffraction at low temperatures, the NaZn_{13}-type cubic symmetry (Fm\overline{3}c) is confirmed below and above \( T_C \), therefore the present first-order transition is unrelated to the structural phase transition and a significant change in volume at \( T_C \) is caused by the change of \( M(T) \) given in Eq. (1). It should be noticed that the coefficient \( k C_{mv} \) of \( 8 \times 10^{-3}/\mu_B^2 \) for \( x = 0.88 \) is comparable to that of \( 5 \sim 10 \times 10^{-3}/\mu_B^2 \) for itinerant-electron metamagnetic Lu(Co_{1-x}Ga_{x})_{2} and Y(Co_{1-x}Al_{x})_{2} compounds. In the present compounds,
TABLE I. Spontaneous magnetization \( M_s \), the Curie temperature \( T_C \), pressure coefficients of the spontaneous magnetization \( d \ln M_s/dP \), and the Curie temperature \( d \ln T_C/dP \), and the ratio \( d \ln T_C/d \ln M_s \) for the La(Fe_{0.88}Si_{0.12})_{13} (Ref. 34), together with those for ordered and disordered Fe_{78}Pt_{22}, and Fe_{65}Ni_{35} alloys (Refs. 48 and 49).

| \( \text{La(Fe}_{0.88}\text{Si}_{1-x})_{13} \) | \( \text{Fe}_{78}\text{Pt}_{22} \) (ordered) | \( \text{Fe}_{78}\text{Pt}_{22} \) (disordered) | \( \text{Fe}_{65}\text{Ni}_{35} \)
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>( M_s (\mu_B) )</td>
<td>2.05</td>
<td>2.15</td>
<td>2.13</td>
</tr>
<tr>
<td>( T_C (K) )</td>
<td>195</td>
<td>510</td>
<td>380</td>
</tr>
<tr>
<td>( d \ln M_s/dP (1/\text{GPa}) )</td>
<td>-0.019</td>
<td>-0.004</td>
<td>-0.007</td>
</tr>
<tr>
<td>( d \ln T_C/dP (1/\text{GPa}) )</td>
<td>-0.46</td>
<td>-0.09</td>
<td>-0.09</td>
</tr>
<tr>
<td>( d \ln T_C/d \ln M_s )</td>
<td>24</td>
<td>23</td>
<td>13</td>
</tr>
</tbody>
</table>

\( ^a \)Reference 34.
\( ^b \)Reference 48.
\( ^c \)Reference 49.

The expansion has been applied to calculate the magnetovolume effects in Fe-Pt and Fe-Ni invar-type alloys.\(^{6,9,42,43}\) According to these results, the magnetic state is also close to the tricritical point.\(^{42}\) Furthermore, a thermal induced first-order transition from the F state with a large volume to the P state with a small volume is derived from the fixed-spin-moment (FSM) band calculation for an ordered Fe₇₅Pt₂₅ invar-type alloy.\(^{32}\) Unfortunately, the first-order transition is depressed by a martensitic transformation\(^{1,2}\) and hence there are no experimental reports on the first-order magnetic phase transition at \( T_C \) for Fe-Pt alloys. It should be noted that the recent FSM band calculation for disordered Fe₇₂Pt₂₈ invar-type alloy also indicates a similar energy barrier between the F and the P states.\(^{43}\) On the other hand, the calculated phase transition for Fe-Ni invar-type alloys is the second order due to an unclear energy barrier in the magnetic free energy.\(^{6,42}\) Accordingly, it is expected that the feature of the magnetovolume effect in the La(Fe₇₁₋ₓSi₁ₓ)₁₃ compounds is similar to that of Fe-Pt rather than that of Fe-Ni invar-type alloys.

One of the most important features of the magnetovolume effects related to the IEM transition is that the pressure dependence of the Curie temperature \( T_C \) is significant, compared with that of the spontaneous magnetic moment \( M_S \).\(^{14,17}\) To compare the pressure effects of the present compounds and those of invar-type alloys, the values of \( M_S \), \( T_C \), pressure coefficients of \( M_S \) and \( T_C \) and the ratio of pressure coefficient of \( T_C \) to that of \( M_S \) for the La(Fe_{0.88}Si_{0.12})_{13} compound,\(^{34}\) ordered and disordered Fe₇₈Pt₂₂, and Fe₆₅Ni₃₅ invar-type alloys\(^ {48,49} \) are listed in Table I. As shown in Table I, for both the ordered and disordered Fe₇₈Pt₂₂ invar-type alloys, \( d \ln T_C/dP \) is one order larger in magnitude than \( d \ln M_S/dP \), while both the pressure coefficients are the same order for Fe₆₅Ni₃₅ invar-type alloy. Accordingly, the ratio of the pressure coefficient of \( T_C \) to that of \( M_S \), \( d \ln T_C/d \ln M_S \), for ordered and disordered Fe₇₂Pt₂₈ invar-type alloys is one order larger than that for Fe₆₅Ni₃₅ alloy. It should be noted that the ratio of the La(Fe_{0.88}Si_{0.12})₁₃ compound is almost the same as that for ordered Fe₇₂Pt₂₈ alloy as seen from the last line in the table, although the former exhibits the first-order and the latter the second-order phase transition. The effect of pressure on \( M_S \) is mainly attributed to the bandwidth narrowing caused by a smaller volume un-
der applied pressure. On the other hand, the Curie temperature strongly depends on the temperature dependence of the magnetic free energy due to the renormalization effect of spin fluctuations given by Eq. (2). Therefore the effect of pressure on also involves the influence of spin fluctuations.

By adding the elastic energy, \(\omega(T)^2/2\kappa\), for the volume change, \(\omega(T)\), and the magnetovolume energy, \(-\omega(T)C_{\text{mv}}(M(T)^2 + \xi(T)^2)\), to Eq. (2), the following relations are derived:

\[-\omega(T) = \kappa P - \kappa C_{\text{mv}}(M(T)^2 + \xi(T)^2)\]  

and

\[\mu_0H = A(T)M + B(T)M^3 + C(T)M(T)^5 - 2\omega(T)C_{\text{mv}}M(T).\]

For the first-order F-P transition, the Curie temperature \(T_C\) is obtained from Eqs. (3) and (4) under the condition that the energy level in the F state is the same as that in the P state. For the second-order transition, on the other hand, \(T_C\) is determined as the temperature where \(dH/dM = 0\). Equations (3) and (4) describe that the renormalization effect related to spin fluctuations for free energy indicates the pressure dependence through the magnetovolume effect. Namely, the spontaneous volume magnetostriction discussed in Eq. (1) reduces the variation of the free energy by the renormalization effect of spin fluctuations. On the other hand, the decrease of volume by hydrostatic pressure enhances the renormalization effect, resulting in the decrease in the Curie temperature. Therefore the significant difference between the magnitude of \(d\ln M_{s}/dP\) and \(d\ln T_C/dP\) implies a strong contribution from the renormalization effect of spin fluctuations, and the influence of spin fluctuations on the magnetovolume effects in the present compound is similar to that in the order and disorder Fe-Pt invar-type alloys, though the direct comparison of the renormalization effect is difficult because of the dependence of \(\xi(T)\) on the microscopic parameters such as a cutoff wave vector of spin fluctuations.

Next, the 3\(d\) band calculation has been applied to examine the relation between the magnetovolume effect and the metamagnetic transition. The projected density of state (DOS) curves in the F state is presented in Fig. 2. The energy scale is shifted so as to the Fermi level \(E_F = 0\). The La5\(d\) and Fe3\(d\) bands are well hybridized, but the main part of the partial DOS of the La5\(d\) is still recognized around +4 eV. The main part of the 3\(d\) DOS in the majority spin band is located below \(E_F\). Furthermore, \(E_F\) lies just at the dip between maxima around +2.0 eV and around -1.8 eV in the minority spin band. It should be noticed that a similar dip structure of DOS around \(E_F\) located between large maxima for Fe-Pt system is connected with the small \(d\ln M_{s}/dP\). In order to confirm the low density of states at the Fermi level, \(\rho(E_F)\), the coefficient of the electronic specific-heat coefficient \(\gamma\) and the high-field magnetic susceptibility \(\chi_{hf}\) have been investigated. The values of \(\gamma\) and \(\chi_{hf}\) for the La(Fe0.888Si0.12)13 together with those for ordered and disordered Fe78Pt22, and Ni65Fe35 invar-type alloys are presented in Table II. As seen in Fig. 2, \(E_F\) of the La(Fe0.888Si0.12)13 is located well above the 3\(d\) majority spin band. According to the first-principles band calculations, \(E_F\) of ordered Fe3Ni and disordered Fe78Ni22 alloys crosses the upper part of majority spin 3\(d\) band, while those of ordered Fe3Pt and disordered Fe25Pt75 alloys are situated the upper edge. In Table II, the value of \(\gamma\) proportional to \(\rho(E_F)\) in the free-electron model exhibits the difference in magnitude, consistent with the calculated results of \(\rho(E_F)\) regardless of the difference in composition and atomic order between the calculations and the experiments for Fe-Pt and Fe-Ni invar-type alloys. The value of \(\chi_{hf}\) is also related to \(\rho(E_F)\) as

\[\chi_{hf} = \chi_{hf}^0\left\{1 + (\chi_{hf}^0)^2 \left((g\mu_B)^2 \frac{\rho_+(E_F)}{\rho_+(E_F)^2} - \frac{\rho_-(E_F)}{\rho_-(E_F)^2}\right)\right\} - \partial I\left|_{M=M_0}\right| H,\]

with

\[\chi_{hf}^0 = (g\mu_B)^2\left\{\frac{1}{\rho_+(E_F)} + \frac{1}{\rho_-(E_F)} - I\right\}^{-1}.\]
where $I$ is the effective exchange integral. The subscripts $+$ and $-$ of $\rho$ indicate the majority and the minority spin bands, respectively. Although this relation is not so straightforward as $\gamma$, the value of $\rho_\gamma(E_F)$ is a leading term for strong ferromagnets in which the majority spin band is situated below $E_F$. Accordingly, $\chi_{\text{f}}$ of the strong ferromagnetic La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ compound and the ordered and disordered Fe$_{78}$Pt$_{22}$ invar-type alloys is smaller than that of the weak ferromagnetic Fe$_{53}$Ni$_{47}$ invar-type alloy.

From the results of the fixed-spin-moment band calculations, it has been pointed out that the feature of paramagnetic DOS is also important to discuss the large volume effect in Fe-Pt and Fe-Ni invar-type alloys.\cite{9,7} Figure 3 shows the DOS curve for the paramagnetic La(Fe$_{0.88}$Si$_{0.115}$)$_{13}$ compound. The general feature of the 3$d$ DOS is relatively similar to that of fcc Fe, ordered Fe$_{3}$Pt, and Fe$_{5}$Ni,\cite{7,9,5} though the bandwidth is different from one another. Especially, a high DOS in the upper part of the 3$d$ band close to the Fermi level is considered as one of the triggers of the magnetic instability in Fe-Pt and Fe-Ni invar-type alloys.\cite{7,9} Furthermore, it has been pointed out that the peak of DOS just above $E_F$, which goes down below $E_F$ by the exchange splitting in the F state, is the origin of the energy barrier between the P and the F states.\cite{9} It should be noticed that the peak of DOS just above $E_F$ is consistent with the negative sign of the mode-mode coupling coefficient $b$ among spin fluctuations discussed in connection with $d\ln T_C/dP$. Namely, the mode-mode coupling coefficient $b$ in Eq. (2) is related to the 3$d$ band structure as follows:\cite{56}

$$b = \frac{1}{16 \rho(E_F)} \left( \frac{(\rho(E_F))}{\rho(E_F)} - \frac{\rho(E_F^\prime)}{3 \rho(E_F)} \right).$$

The peak of the DOS just above $E_F$ tends to make the sign of $b$ negative.\cite{56} Therefore it is concluded these features for the large magnetovolume effects and the first-order magnetic phase transition are confirmed in the band structures of the La(Fe$_{0.88}$Si$_{0.115}$)$_{13}$, though a quantitative uncertainty of the peak height of the calculated DOS is involved due to a large number of atoms in the formula unit cell.

**IV. CONCLUSION**

In order to discuss the correlation between the itinerant-electron metamagnetic (IEM) transition and the large magnetovolume effects in the La(Fe$_{0.88}$Si$_{0.115}$)$_{13}$ compounds, calculated 3$d$ band structures of the La(Fe$_{0.88}$Si$_{0.115}$)$_{13}$ compound in the ferromagnetic and the paramagnetic states are compared with those of Fe-Pt and Fe-Ni invar-type alloys. A significant magnetovolume effect is observed in La(Fe$_{0.88}$Si$_{0.115}$)$_{13}$ not only in the range $x \geq 0.84$ at the first-order ferromagnetic-paramagnetic transition at $T_C$, but also in the range $x < 0.84$, where the transition at $T_C$ is of the second order. A large pressure dependence of the Curie temperature $T_C$ compared to that of the spontaneous magnetization $M_S$ is observed in $x = 0.88$, which is similar to the magnetovolume effects in the Fe$_{78}$Pt$_{22}$ invar-type alloy. The band calculations reveal that the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ compound is in a strong ferromagnetic state, consistent with the experimental results of the electronic specific-heat coefficient $\gamma$ and the high-field magnetic susceptibility $\chi_{\text{f}}$. Furthermore, the feature of majority spin band in the ferromagnetic state is similar to that of ordered and disordered Fe-Pt invar-type alloys, and the feature of the 3$d$ band in the paramagnetic state is close to the condition for the inducement of magnetic instability, accompanied by the first-order magnetic transition.

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*Electronic address: afujita@material.tohoku.ac.jp

1Present address: Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China.


A. Fujita, K. Fukamichi, J.-T. Wang, and Y. Kawazoe