

Thermally activated itinerant metamagnetic transition in LaFe_{11.7}Si_{1.3}

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We have investigated the process of a metamagnetic transition (MT) between the ferromagnetic and paramagnetic states in the LaFe_{11.7}Si_{1.3} compound, which has both giant magnetocaloric and large magnetovolume effects. The nucleation in MT, which indicates the coexistence of two phases, can be obviously activated by thermal fluctuation in the presence of magnetic fields. The experimental magnetization curves are well reproduced based on the itinerant metamagnetism theory considering thermal activation, and are largely different from the athermal MT. The critical nucleation volume for the phase transition approximates to 300 nm³, and the surface energy to prevent MT is about 2×10^{-4} J/m².

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Recently, the giant magnetocaloric and large magnetovolume effects have attracted much attention.¹⁻⁷ According to the Maxwell relation $(\partial S / \partial H)_T = (\partial M / \partial T)_H$, a large change of magnetic entropy requires a strongly temperature-dependent magnetization.^{8,9} This leads researchers to seek materials that show a first-order magnetic transition associated with an abrupt magnetization change at Curie temperature. The recently discovered giant magnetocaloric effect is associated with the magnetic first-order transition.¹⁻⁵ Furthermore, a remarkable magnetovolume effect is also accompanied by the magnetic first-order transition.^{6,7} In Fe-based alloys, the temperature dependence of the spontaneous magnetostriction compensates the lattice expansion due to anharmonic atomic vibration, resulting in almost zero thermal expansion, i.e., the Invar effect in these alloys. Therefore, it is fundamentally and practically important to fully understand the nature of the magnetic first-order transition in order to design better magnetic materials.

Conventionally a transition from a magnetically ordered to disordered state is second order.¹⁰ The magnetic first-order transition from a paramagnetic state of itinerant electrons into a magnetically ordered state was first predicted by Wohlfarth and Rhodes¹¹ based on the Stoner model, i.e., itinerant metamagnetic transition (MT). The rigorous conditions for the appearance of MT were formulated by Shimizu,¹² and the theory of itinerant metamagnetism considering spin fluctuation has been reviewed by Levitin and Markosyan.¹³ As a typical example, we consider the transition between the paramagnetic and ferromagnetic states in the following. MT can be discussed in terms of Landau-Ginzburg expansion of the free energy density f by including the renormalization effect associated with spin fluctuation as^{13,14}

$$f(M) = \frac{1}{2}aM^2 + \frac{1}{4}bM^4 + \frac{1}{6}cM^6, \quad (1)$$

where parameters a , b , and c depend on temperature and pressure according to Landau-Ginzburg theory, and they are essentially correlated with the density of states and its derivative around the Fermi energy in itinerant metamagnetism.¹³ The conditions for the magnetic first-order

transition are $a > 0$, $b < 0$, $c > 0$, and $\frac{3}{16} < ac/b^2 < \frac{9}{20}$.¹² In this case, $f(M)$ shows a double-minimum structure. The transition can be triggered by temperature, magnetic field, and/or pressure. As mentioned above, both the giant magnetocaloric and large magnetovolume effects are related to MT.

The magnetic equation of state for M and H is given by

$$H = \frac{\partial}{\partial M} f(M) = aM + bM^3 + cM^5. \quad (2)$$

When H is applied to the samples, f will show a maximum f_3 between two minima f_1 and f_2 . For simplification, we use 1, 2, and 3 to represent the states with f_1 , f_2 , and f_3 , respectively. States 1 and 2 correspond to the paramagnetic and ferromagnetic states, respectively. With H increasing (decreasing) to a critical value H_{c1} (H_{c2}), an inflection point replaces the maximum. Thus, a hysteresis loop appears in the first quadrant and the magnetization jumps discontinuously to a finite value at H_{c1} (H_{c2}). In the process of MT, a metastable phase first goes through *supercooling*, then changes to a new phase suddenly. However, the effect of thermal activation on MT is not considered in Eq. (2). The MT process discussed above is only true for cases at zero temperature or athermal-characterized transition.¹⁵ In general, when a system is externally driven through a first-order phase transition, the response to the external control parameter is determined by the characteristics of the energy barriers separating the two phases. Only when temperature acts as an external field and the thermal activation does not play an important role, the system remains in a given configuration as long as the state corresponds to a free energy local minimum. But, thermal activation is usually considered essential for a phase transition. Therefore, it is necessary to make clear what happens in the process of MT at a finite temperature.

To check the effect of the thermal activation on MT, one should know the time dependence of magnetization. The Arrhenius-Néel statistical switching model

$$\tau = \tau_0 \exp(E/k_B T) \quad (3)$$

is justified for magnetic systems by Brown,^{16,17} where τ is the mean waiting time before the jump, $1/\tau_0$

$= 10^{10} - 10^{13} \text{ s}^{-1}$ is the attempt frequency,^{17,18} k_B is the Boltzmann constant, and E is the energy barrier to overcome. However, the relaxation of magnetization was studied only for the superparamagnetic system¹⁸ and the permanent magnet.^{19,20} Here, we give an expression of thermal activation for MT. The numbers of the volume element in state 1 and 2 are noted as N_+ and N_- , respectively. $N_+ + N_- = N$ is constant. The energy barriers for jumping from state 2 to 1 and that from state 1 to 2 are $E_{21} = (f_3 - f_2)v$ and $E_{12} = (f_3 - f_1)v$ (v is the volume element), respectively. So, the variation of N_+ with time is

$$\frac{dN_+}{dt} = -\frac{N_+}{\tau^+} + \frac{N_-}{\tau^-}, \quad (4)$$

where $\tau^+ = \tau_0^+ \exp(E_{12}/k_B T)$ and $\tau^- = \tau_0^- \exp(E_{21}/k_B T)$. Both τ_0^+ and τ_0^- are to be determined from microscopic theories, which is so difficult that no satisfactory results have been achieved up to now.^{16,17,19} However, τ_0^+ has been found to be approximately equal to τ_0^- .^{18,21} Thus, we assume $\tau_0^+ = \tau_0^- = \tau_0$ for simplicity. After the integration of Eq. (4), we get

$$N_+(t) = \frac{1}{\tau^+ + \tau^-} \left[N\tau^+ + N\tau^- \exp\left(-\frac{t}{\tau^+} - \frac{t}{\tau^-}\right) \right]. \quad (5)$$

Noting that

$$M(t) = M_1 \frac{N_+}{N} + M_2 \frac{N_-}{N}, \quad (6)$$

we get the time dependence of M as follows,

$$M(t) = \frac{M_1 \tau^+ + M_2 \tau^-}{\tau^+ + \tau^-} + \frac{(M_1 - M_2) \tau^-}{\tau^+ + \tau^-} \exp\left(-\frac{t}{\tau^+} - \frac{t}{\tau^-}\right), \quad (7)$$

where M_1 and M_2 are the magnetization at points 1 and 2, respectively. Both M_1 and M_2 are time independent.

$\text{La}(\text{FeSi})_{13}$ compounds with low silicon content show a thermally induced first-order phase transition at the Curie temperature and a field-induced itinerant MT above the Curie temperature. Both giant magnetocaloric and large magneto-volume effects are found in $\text{La}(\text{FeSi})_{13}$ compounds with MT.^{2,6,7} Meanwhile, it is noteworthy that MT in $\text{La}(\text{FeSi})_{13}$ compounds is not blurred by a martensitic transition as present, e.g., in corresponding FePt compounds.^{6,7} Therefore, we choose the $\text{La}(\text{FeSi})_{13}$ compound as the material to study MT extensively.

The sample with the nominal composition $\text{LaFe}_{11.7}\text{Si}_{1.3}$ was prepared by arc melting and the following heat treatment. As confirmed by x-ray diffraction, the sample is single phase with the NaZn_{13} -typed structure. The sample was milled to the shape of prolate spheroid with a polar radius about 1.00 mm and an equatorial radius about 0.72 mm. The demagnetization factor D is about 0.25 and the mass of the sample is about 16.5 mg. Thus, the magnetic field H suffered by the sample equals to $H_{\text{appl}} - DM$ (H_{appl} is the applied magnetic field). The magnetic measurement was carried out using dc extraction magnetometry of PPMS-14T (Quantum Design). For the change of H_{appl} , the approach mode of Linear and end mode of Persistent were used at a rate about

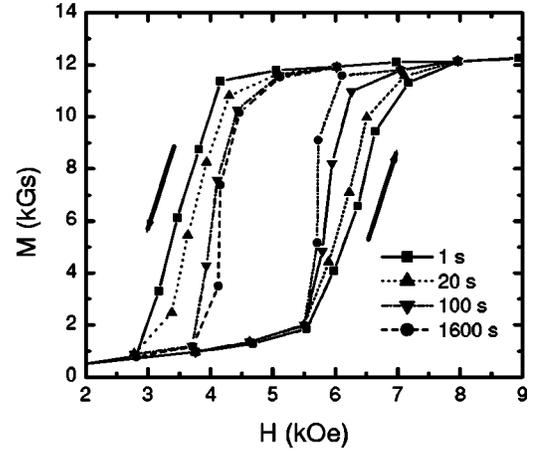


FIG. 1. The magnetization curves with increasing and decreasing magnetic field at 194 K for $\text{LaFe}_{11.7}\text{Si}_{1.3}$ compounds. t_w^e (shown in figure) is the time at which magnetization is measured after the field reaching the set point.

42.6 Oe/s. Thus, there was roughly a delay of 20 s (i.e., switch cooling time) between the magnet reaching the set field and the criterion determining whether H_{appl} has reached the set point. The Curie temperature of the sample is about 193 K under the applied magnetic field of 0.1 kOe. The time dependence of magnetization was obtained by measuring the magnetization at a time t_w^e (superscript e denotes the time for experiment) after H_{appl} had increased (decreased) directly from 0 (50) kOe to the target value. It took about 2 s to make a measurement. The magnetization curves and the time dependence of magnetization were measured at 194 K.

Figure 1 shows the magnetization curves for increasing and decreasing field. For clarity, Fig. 1 only gives the magnetization curves with typical $t_w^e = 1, 20, 100,$ and 1600 s. A hysteresis loop was found in the first quadrant, which is a typical behavior for MT between paramagnetic and ferromagnetic state.^{12,13}

As an example, Fig. 2 shows the time dependence of magnetization at $H_{\text{appl}} = 4$ and 5 kOe after being fully magnetized at $H_{\text{appl}} = 50$ kOe. The magnetization varies with time explic-

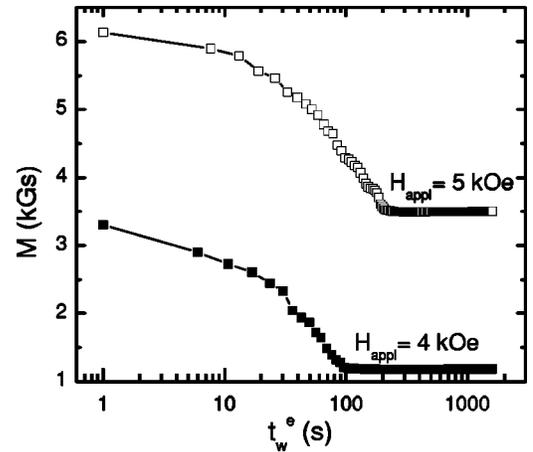


FIG. 2. The time dependence of magnetization at $H_{\text{appl}} = 4$ and 5 kOe after decreasing H_{appl} from 50 kOe.

ity. The relaxation of magnetization under a constant H_{appl} means the occurrence of a phase transition. Although the variation is very large as shown in Fig. 2, the magnetization does not decrease directly to the value corresponding to the paramagnetic state. For a continuous transition, thermal activation makes the complete transition. Therefore, the relaxation of magnetization in the sample reflects the thermally activated nucleation of the new phase. As shown in Fig. 1, the ferromagnetic and paramagnetic phases nucleate in the magnetizing and demagnetizing processes, respectively. It is a spatially phase-segregated state where two phases coexist within the sample. The same result is observed in the pressure-induced MT.⁵

The condition of Eq. (7) is that H is suddenly switched to the target value. However, in the experiment, H_{appl} changes continuously. Although the solid points shown in Fig. 1 were obtained at $t_w^e = 1$ s, they are not the same points obtained simply by Eq. (7). Meanwhile, two phases coexist during the magnetization relaxation, so the effect of dipole-dipole interaction on the relaxation must be considered. As reported in Refs. 18 and 21, the dipolar interaction may slow down the relaxation. For simplicity, the dipolar interaction is approximated by the demagnetization field DM . As shown in Fig. 1, the energy barrier to be thermally overcome is increased as M varies with t , which also slows down the relaxation. For example, as shown in Fig. 2 H increases with the decrease of M , which results in the rise of energy barrier. Therefore, the experimental variation of M with t cannot be directly fitted using Eq. (7). Fortunately, the magnetization changes very slowly with time after $t_w^e > 1000$ s in this experiment, which means that H is approximately time independent for $t_w^e > 1000$ s. To ignore the effect of demagnetization field on magnetic relaxation, the magnetization curves measured for $t_w^e = 1600$ s is used to get information on the MT. On the other hand, the error originating from the mode of field change is depressed in this case.

For a given a , b , c , and τ , we can calculate the magnetization curves with different t_w^c (the superscript c denotes the time for calculation) using Eqs. (2) and (7). In other words, we can use Eqs. (2) and (7) to simulate the experimental magnetization curves shown in Fig. 3. However, we must give a value to τ_0 before the simulation because τ is determined by both v and τ_0 . So the parameters a , b , c , and v can be obtained after the simulation with a given τ_0 . It is important to note that only a , b , and c can be uniquely obtained from the experimental curves, whereas the parameter v is uncertain in the simulation due to uncertainty of τ_0 .^{17,18} After simulating the experimental magnetization curves with $t_w^e = 1600$ s as shown in Fig. 3, we obtain the parameters $a = 4.4$ Oe/G s, $b = -9.4 \times 10^{-8}$ Oe/G s³, and $c = 4.6 \times 10^{-16}$ Oe/G s⁵. And we can also get $v = 300$ nm³ for $\tau_0 = 10^{-11}$ s. The simulated magnetization curves shown in Fig. 3 are that for $\tau_0 = 10^{-11}$ s. It is shown that the experimental curves with $t_w^e = 1600$ s are well fitted by the calculated ones with $t_w^c = 1600$ s. The experimental magnetization curves with $t_w^e = 1600$ s can also be fitted by other pairs of v and τ_0 for the obtained a , b , and c . The relationship between v and τ_0 can be formulated as $v = 39.0 - 23.7 \log_{10} \tau_0$. It is also shown that the variation of v strongly affects the value of τ_0 . The variation of v is about 120 nm³ when τ_0 varies from

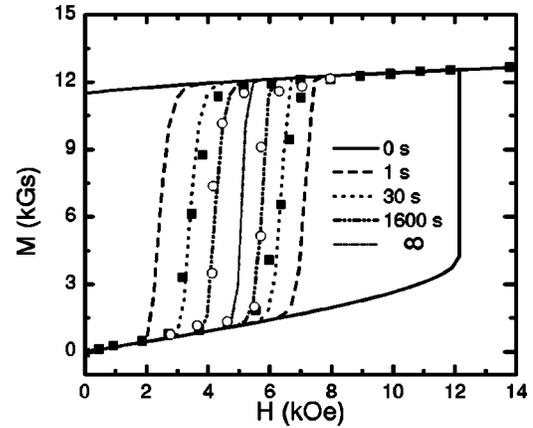


FIG. 3. The calculated magnetization curves (lines) at a given value of t_w^e (shown in figure). The solid square (open circle) represents the experimental ones measured at $t_w^e = 1$ s (1600 s).

10^{-14} to 10^{-9} s. Therefore, v around 300 nm³ is reasonable for the value range of τ_0 as given in Refs. 17 and 18. For the athermal case, after the sample is magnetized to saturation, the sample remains in the ferromagnetic state even at zero field, which is reasonable because the Curie temperature measured at $H_{\text{appl}} = 0.1$ kOe is 193 K. Similar behavior has been found in the MT of Gd₅Ge₄.⁴ According to Eq. (2), the calculated H_{c1} and H_{c2} for the athermal case are -2.2 and 12.2 kOe, respectively. Even though the value of H_{c1} is replaced by zero, the value of $H_{c2} - H_{c1}$ for the athermal case is much larger than that for the experimental one. Therefore, the thermal activation affects MT strongly.

As shown in Fig. 3 there is little thermal activation at H around 5.0 kOe for both calculated and experimental curves, which is due to the small value of $\Delta f = |f_1 - f_2|$ in addition to the large energy barrier.^{22,23} When H decreases (increases) from 5.0 kOe for the field-decreasing (-increasing) curve, the value of Δf becomes large, which leads to the supercooling of the ferromagnetic (or paramagnetic) phase for the athermal MT. However, at the field around 4 (or 6) kOe for the branch curve with field decreasing (or increasing), the energy barrier for MT is about 25.7 (or 27.2) $k_B T$. According to Eq. (3), the mean waiting time for the activation of MT is about 1.5 (or 6.5) s in this case. Therefore, the experimental curves as shown in Fig. 3 are observed. Experimentally, H_{appl} always changes at a finite rate. Before the target value (e.g., $H_{\text{appl}} = 4$ kOe) is reached, the relaxation during decreasing H from 5 kOe is already effective, which is particularly important when considering small waiting time t_w^e . Furthermore, the value of $t_w^c - t_w^e$ is about 30 s after considering the switch cooling time, which well corresponds to the full symbols with $t_w^c = 30$ s as presented in Fig. 3.

According to classical nucleation theory, a phase transition is initiated by the formation of a critical nucleus. The obtained volume element v can be regarded as the critical volume of nucleus. Assuming a shape of sphere for the volume element, the critical radius r_c of the nucleation is about 4.2 nm, which is much smaller than the grain size (about 10 μm) of the sample. On the other hand, r_c can be deduced from^{22,24}

$$E = 4\pi r^2 \sigma - \frac{4}{3}\pi r^3 \Delta f, \quad (8)$$

where σ is the surface energy between the nucleated seed and the host crystal. Thus, r_c is equal to $2\sigma/\Delta f$ for the growth of new phase within the *supercooled* phase.^{22,24} For smaller radii, the surface energy depresses the nucleation of the new phase if the size of the nucleus is below the critical value. The values of Δf around $H=4.0$ kOe for decreasing field and 6.2 kOe for increasing field are about 98 and 95 kJ/m³, respectively. So, σ is about 2×10^{-4} J/m². What is the contribution to σ ? Following the transition from the ferromagnetic to paramagnetic state, the lattice constant changes significantly in the samples.^{2,6,7} Therefore, we can conclude that σ mainly arises from the surface tension.

In summary, for the MT between paramagnetic and ferromagnetic state in the LaFe_{11.7}Si_{1.3} compound, the coexistence of two phases is found. The nucleation in the MT can be

induced by thermal activation. In addition to the small value of Δf , the energy barrier at $H=5$ kOe is so large that the mean waiting time for activation is unrealizable within the age of the Universe. However, the energy barrier becomes so small at the field far away from H_{c1} or H_{c2} that MT can be thermally activated, which results in the experimental hysteresis loop largely different from that for the athermally characterized transition. The critical size of the nucleation is about 4.2 nm. For smaller radii of nucleation, the large surface energy forces new phase bubble to disappear. The larger radii of the nucleation of new phase results in the full completion of the MT. Whether the results presented in this paper can be generalized to other experimental systems with the MT is still an open question, which will be interesting to analyze further.

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