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The spike in the relation between entropy change and temperature in $LaFe_{11.83}Si_{1.17}$ compound

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Abstract

$LaFe_{11.83}Si_{1.17}$ compound shows a first-order transition from paramagnetic to ferromagnetic state. When measurement is carried out from low to high temperature in an increasing field, there is a spike of 51 J/kg K at 174.8 K, followed by a plateau of 20 J/kg K in the curve of entropy change versus temperature determined by the Maxwell relation. However, the nature of the spike is fictitious, which is caused by an obvious superheat of the ferromagnetic state when the Maxwell relation or the Clausius–Clapeyron equation is used to evaluate the entropy change.

Keywords: Magnetic entropy change; Maxwell relations; Magnetic first-order transition

1. Introduction

Since a large magnetic entropy change near room temperature was found in $Gd_5(Si, Ge)_4$ compounds in 1997 [1,2], the investigations on room temperature magnetic refrigerant have attracted much attention. A magnetic first-order transition (MFOT) is a characteristic of the materials showing a large magnetocaloric effect (MCE), such as $R_5(Si, Ge)_4$ [1,2], MnAs [3,4], $La(Fe,Si)_{13}$ [5,6], MnFePAs [7] and Ni_2MnGa [8–10] based compounds. The MCE can be measured by the adiabatic temperature change or the isothermal magnetic entropy change ($\Delta S(T, \Delta H)$). For convenience and due to the relatively small experimental error, $\Delta S(T, \Delta H)$ is usually recorded as follows using the integrated Maxwell relations:

$$\begin{aligned}\Delta S(T,\Delta H) &= \int_{H_1}^{H_2} (\partial M(T,H)/\partial T)\mathrm{d}H \\ &\simeq [1/(T_2-T_1)] \\ &\quad\times \int_{H_1}^{H_2} [M(T_2,H)-M(T_1,H)]\mathrm{d}H \qquad (1)\end{aligned}$$

where $T=(T_1+T_2)/2$, $\Delta H=H_2-H_1$ and H_1 is usually chosen as zero (in this paper $H_1=0$). The relative error in $\Delta S(T, \Delta H)$ was discussed considering the field interval δH and temperature interval $\delta T(=T_2-T_1)$ [11]. The argument for the Maxwell relations valid in estimating $\Delta S(T, \Delta H)$ for $Gd_5(Si, Ge)_4$ confirmed that both the Maxwell relations and Clausius–Clapeyron equation can be used to calculate $\Delta S(T, \Delta H)$ accompanied by the MFOT [12–16]. Up to now, several phenomenological models have been developed to describe the temperature dependence of $\Delta S(T, \Delta H)$ at a constant ΔH for the MFOT [16–21]. In these models, a nearly plateau-like temperature dependence of $\Delta S(T, \Delta H)$ was predicted, which is well consistent with most of the experimental results. However, we recently found an unexpectedly large spike on the plateau-like part in the curve of $\Delta S(T, \Delta H)$ versus T for $La(Fe, Si)_{13}$-type materials.

In fact, the unexpected spike is visible in several reports concerning $MnAs_{1-x}Sb_x$ [3], $La(Fe, Si)_{13}$ [22], $Gd_5(Si, Ge)_4$ [23] and Mn_3GaC [21] compounds. Even a huge spike-like $\Delta S(T, \Delta H)$ about 267 J/kg K is observed in MnAs [4]. In Ref. [12], such behavior is supposed to occur in any compound undergoing the MFOT when the Maxwell relation is used to evaluate $\Delta S(T, \Delta H)$. However, three

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different explanations for the spike are given in the literature [3,21,24]. As in Ref. [3] the spike is probably an artifact because the summation with a finite field interval δH, rather than integration, is employed in the evaluation procedure, while Yu et al. [21] opined that the spike originates from the interplay between the temperature-induced and the field-induced transitions. Recently, we found that the spike is caused by inappropriately using the Maxwell relation for the system with the coexistence of ferromagnetic and paramagnetic phases [24]. Therefore, it is necessary to research into the physical origin of the spike. In this work, efforts are made to probe into the feature and origin of the spike.

2. Experiment

The nominal $LaFe_{11.83}Si_{1.17}$ compound was prepared by first arc melting the constituent metals and then annealing at 1323 K for 7 weeks. A nearly single $NaZn_{13}$-type phase in the sample was confirmed by the results of X-ray diffraction. The magnetic measurements were performed on a commercial MPMS-7 (Quantum Design) superconducting quantum interference device magnetometer. $\Delta S(T, \Delta H)$ was obtained using Eq. (1). The isothermal variations of the magnetization with the applied magnetic field, i.e. magnetization curves, were measured beginning at 163 K and ending at 200 K with an increasing step of ~0.5 K. Because of the phase transition with temperature hysteresis ~4 K, the overshooting temperature was controlled under 0.1 K. Thus, the error in $\Delta S(T, \Delta H)$ resulted from the temperature overshooting being small. At each temperature, the magnetization was measured under several cycles of the field variation. For convenience, the magnetization curve measured by initially increasing the field from 0 to 5 T was termed the initial curve, the magnetization curve obtained by subsequently decreasing the field from 5 to 0 T was called the 1st H reduction curve, the magnetization curve measured by secondly increasing the field from 0 to 5 T was labeled 2nd H increase curve, the magnetization curve obtained by the following field decrease was called 2nd H reduction curve, etc. The isofield magnetization was measured by increasing the temperature (except otherwise specified). The phase transition temperature $T_C(H)$ was where the value of $(\partial M/\partial T)_H$ reached its maximum. The error in $T_C(H)$ was estimated at ~1 K.

3. Results and discussion

Figs. 1(a) and (b) show some typical initial magnetization and 1st H reduction magnetization curves, respectively. The two-step transition as observed at 175 K in Fig. 1(a) is probably caused by the inhomogeneity of specimens. Figs. 2(a) and (b) exhibit the magnetic entropy change as a function of temperature at a constant ΔH obtained from initial magnetization curves and 1st H reduction ones, respectively. There are spikes obviously shown at 174.8 K in Fig. 2(a), but not in Fig. 2(b). All the curves of $\Delta S(T, \Delta H)$ are identical for the magnetization curves measured with H reduction. The curve of $\Delta S(T, \Delta H)$ for 2nd H increase magnetization is identical to the 1st H increase, except that it is shifted to low temperature by ~1 K compared with that for the initial one, and is the same as those for the succedent H increase ones. Thus, the spikes in $\Delta S(T, \Delta H)$ curves depend on the direction of the field variation.

In Ref. [11], the error in $\Delta S(T, \Delta H)$ is estimated at ~30% above the transition temperature. As an example, for $\Delta H = 2$ T, the values of the spike and the plateau shown in Fig. 2(a) are about 51 and 20 J/kg K, respectively. Therefore, the spikes are not originated from the measuring error. As shown in Fig. 1(a), it is the large difference in initial magnetization curves between 174 and 176 K that leads to the spikes as shown in Fig. 2(a). Fig. 3 shows the variation of the spike value ΔS_{sp} with δT at $\Delta H = 3$ T; here the initial temperature is 174 K. ΔS_{sp} decreases rapidly as δT increases to 3 K, and then it decreases slowly after 3 K. It is noticed that for $\delta T \geqslant 3$ K ΔS_{sp} is slightly larger than the value of the plateau. In other words, for a large δT (>2 K) the spike is artificially weakened. As reported in Ref. [3], the spike value should be related to δH. However, ΔS_{sp} is δH independent as long as δH is not large enough to make Eq. (1) invalid in this work. Fig. 4 shows the dependence of ΔS_{sp} on ΔH. ΔS_{sp} increases rapidly as ΔH increases to

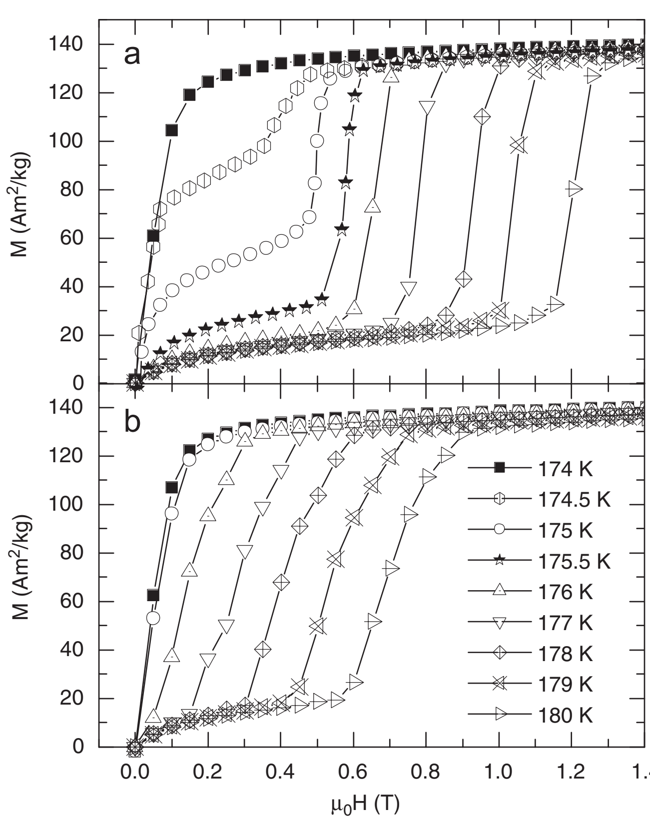

Fig. 1. The initial magnetization (a) and 1st H reduction magnetization (b) curves of $LaFe_{11.83}Si_{1.17}$ at some typical temperature.

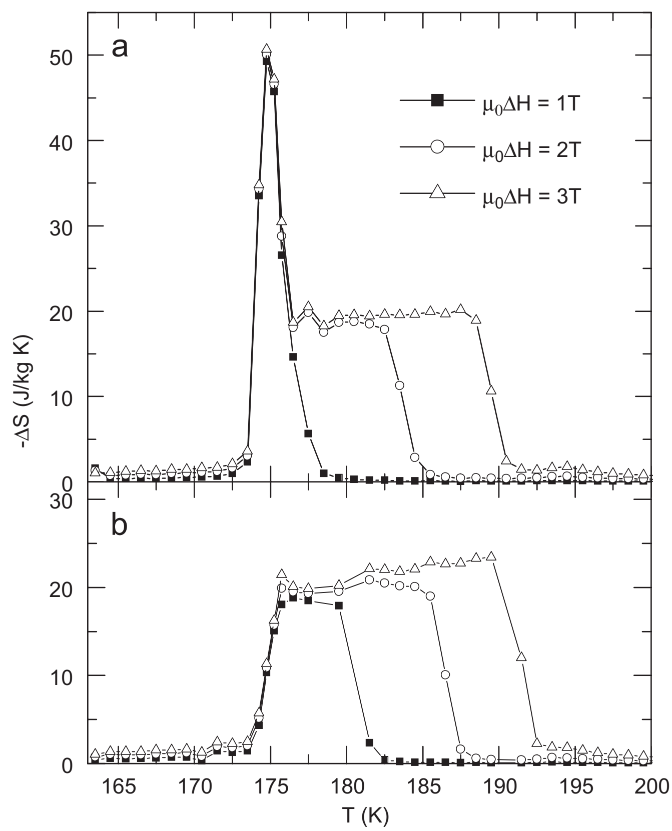

Fig. 2. Entropy change $\Delta S(T, \Delta H)$ for $LaFe_{11.83}Si_{1.17}$ calculated by the integrated Maxwell relation from initial magnetization curves (a) and 1st H reduction ones (b).

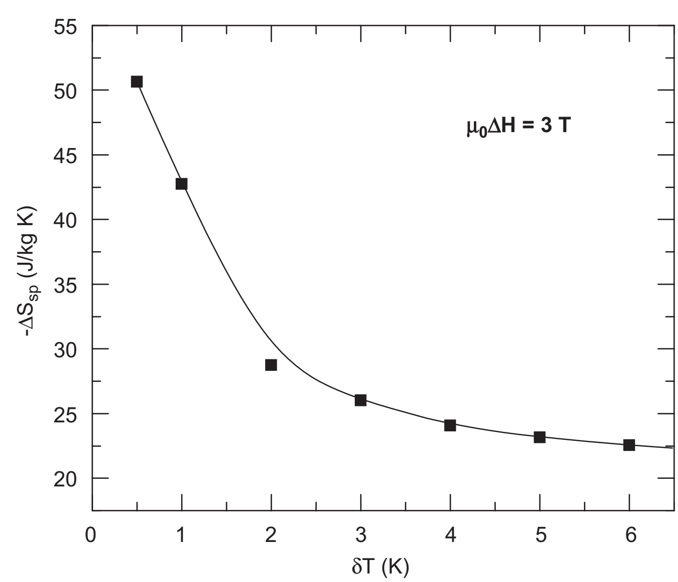

Fig. 3. The variation of ΔS_{sp} with δT at $\Delta H = 3\,T$ for $LaFe_{11.83}Si_{1.17}$, the initial temperature is 174 K.

0.8 T, and then it is nearly saturated after $H > 0.8\,T$. Thus, ΔS_{sp} is almost ΔH independent after the phase transition is nearly completed at $H > 0.8\,T$. Therefore, the spike is not caused by the temperature interval δT or field interval δH.

Fig. 5 shows the field dependence of transition temperature T_C. For $H > 0.8\,T$, T_C increases linearly with a slope $(\Delta T_C/\Delta H)$ of 7 K/T as increasing field, but it remains almost unchanged for $H < 0.8\,T$. As mentioned in the experimental part, the error in determining T_C is ~1 K. Thus, for $H < 0.8\,T$, the value of $\Delta T_C/\Delta H$ is less than 1.3 K/T. According to the Clausius–Clapeyron equation $\Delta S(T, \Delta H) = (\Delta H \Delta M)/\Delta T_C = \Delta M/(\Delta T_C/\Delta H)$, it is the very small value $\Delta T_C/\Delta H$ at about 175 K for $H < 0.8\,T$ that brings about the existence of spike. The small value of $\Delta T_C/\Delta H$ can approximately be used in the case of H increase due to the measurement being carried out in temperature-increasing mode. When ΔM obtained from the magnetization curves [12,18] and $\Delta T_C/\Delta H = 1.3\,K/T$ are used, $-\Delta S(T, \Delta H)$ is estimated to be 0, 17, 50, 70 and 15 J/kg K at 174, 174.5, 175, 175.5 and 176 K, respectively. The value of the plateau is about 15 J/kg K according to the Clausius–Clapeyron equation. Therefore, within the experimental error, the spike behavior obtained by the integrated Maxwell relation (as shown in Fig. 2a) is the same as that obtained by the Clausius–Clapeyron equation.

Note that all discussion about the spike made in Ref. [12] and the subsequent comments [13–15] are not conclusive at all, and the behavior of the spike is not observed in any direct measurement [11,12,25]. However, the plateau-like $\Delta S(T, \Delta H)$ curves obtained from the magnetization data agree well with those obtained directly from calorimeters [6,11,12,25,26]. Thus, it is reasonable to believe that the results shown in Fig. 2(b), but not those shown in Fig. 2(a), are correct. Furthermore, according to $\Delta S(T, \Delta H) = S(T, H) - S(T, 0)$, the maximum $\Delta S(T, \Delta H) \simeq 20$ J/kg K should be equal to the entropy difference between ferromagnetic and paramagnetic states. As a result, there is no reason for the spike to have such a high value.

In view of the refrigerating power, i.e. the integration value, A, of $\Delta S(T, \Delta H)$ with respect to temperature, the

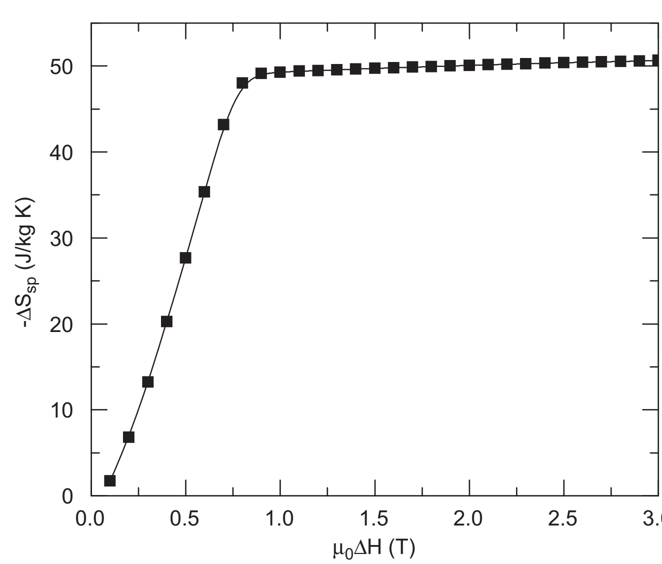

Fig. 4. The dependence of ΔS_{sp} on ΔH for $LaFe_{11.83}Si_{1.17}$.

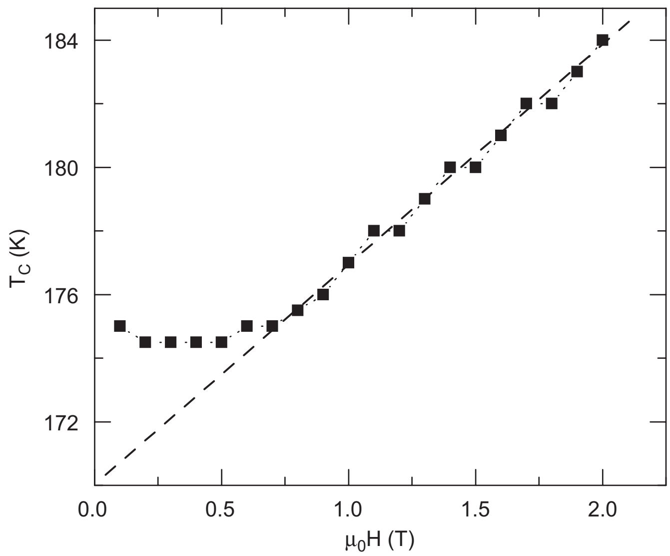

Fig. 5. The field dependence of transition temperature T_C for $LaFe_{11.83}Si_{1.17}$.

value of A for H increasing is the same as that for H decreasing within the experimental error for the titled compound. For example, A is about 123, 262 and 403 J/kg as shown in Fig. 2(a), and 116, 253 and 392 J/kg as shown in Fig. 2(b) for $\Delta H = 1$, 2 and 3 T, respectively. When the curve of $\Delta S(T, \Delta H)$ as shown in Fig. 2(a) is broadened to low temperature by replacing the spike with a plateau of 20 J/kg K and keeping A unchanged, $\Delta S(T, \Delta H)$ will increase rapidly at 170 K. It is well consistent with the linearly extrapolated T_C of 170 K at $H = 0$ as shown in Fig. 5. Therefore, the appearance of the spike can be explained only by suppressing the low-temperature part $\Delta S(T, \Delta H)$ up to around 175 K.

How does this behavior occur? The small $\Delta T_C/\Delta H$ in the vicinity of $T_C(0)$ as shown in Fig. 5 reminds us of the supercooling/superheating phenomenon.

The itinerant-electron magnetism is characteristic of $LaFe_{11.83}Si_{1.17}$ compound. For an itinerant-electron system, the MFOT is closely related to the double minima of the paramagnetic state (f_{PM}) and the ferromagnetic state (f_{FM}) in the magnetic-free energy as a function of magnetization, which results in a magnetic loop in the first quadrant [27–30]. In the vicinity of the intrinsic transition temperature ${}_IT_C$, i.e. the temperature of $f_{FM} = f_{PM}$ under zero field, the initial state of the sample is determined by the history of temperature and/or field variation (the schematic can be found in Figs. 28 and 29 in Ref. [27]). In other words, the metastable ferromagnetic (paramagnetic) phase first goes through superheating (supercooling), then changes to the target phase suddenly. For the titled compound, T_C at 0.01 T is about 4 K larger than that obtained by measuring $M(T)$ with the decreasing temperature, which confirms the existence of the superheating/supercooling of magnetic state.

The zero-field superheated (supercooled) ferromagnetic (paramagnetic) state ends at T_C^h (T_C^c), and $T_C^h > {}_IT_C > T_C^c$. The value of T_C^h is about 176 K for the titled compound. Here, we must mention that the ferromagnetic and paramagnetic states coexist at 175 K as shown in Fig. 1(a), which is mainly caused by thermal activation [30]. In the following part, the effect of thermal activation on the phase transition is omitted for a clear description. For convenience, at a given temperature we define H_{C1} and H_{C2} as the fields of paramagnetic-to-ferromagnetic and ferromagnetic-to-paramagnetic phase transitions, respectively. H_{C1} is larger than H_{C2}. Both H_{C1} and H_{C2} increase monotonically from zero to a large value with the increasing temperature [27–30]. In this work, any H-increasing magnetization curve, which is characterized by H_{C1} for the paramagnetic original state in the temperature range of T_C^c–T_C^h, is substituted by ferromagnetic initial magnetization curve due to the superheat of ferromagnetic state (e.g. the zero-field ferromagnetic state shown at 174 K). Thus, a large difference in H-increasing magnetization curves is generated between the temperatures of 174 and 176 K. In other words, $H_{C1}(T)$ increases suddenly from 0 to $H_{C1}(T_C^h)$ as the temperature increases to T_C^h.

However, for the H-decreasing magnetization curves reflected by H_{C2}, the spike does not appear because H_{C2} increases continuously with temperature increase through T_C^h as shown in Fig. 1(b). For the case of supercooled paramagnetic state, i.e. measured with the decreasing temperature, no spike can be expected because the supercooling of paramagnetic state will be destroyed by the applied field.

It is well known that the Clausius–Clapeyron equation as well as the Maxwell relation are derived from the condition $G(1) = G(2)$, where $G(i)$ is the Gibbs free energy of the corresponding phase i (= 1 or 2). Therefore, they cannot be applied to the case for H increase or reduction where the field (and temperature) hysteresis exists. Theoretically, using the Maxwell relation, ΔS can be obtained from the anhysteresis $M(H)$ curves characterized approximately by the average of H_{C1} and H_{C2}, i.e. H_{CI}. Technically, ΔS can also be obtained from the experimental $M(H)$ curves for H increase (or reduction) only when the area enclosed by the curves with $H_{C1}(T_1)$ and $H_{C1}(T_2)$ (or $H_{C2}(T_1)$ and $H_{C2}(T_2)$) is equal to that with $H_{CI}(T_1)$ and $H_{CI}(T_2)$, which is nearly satisfied in most experiments. In this work, due to the superheating of ferromagnetic state, the $M(H)$ curve with a small value of H_{C1} is unmeasurable. Thus, the spike is caused by mistakenly using the Maxwell relation as well as the Clausius–Clapeyron equation.

In summary, the curves of $\Delta S(T, \Delta H)$ versus T show a spike of about 51 J/kg K at 174.8 K, followed by a plateau about 20 J/kg K in the measurement with increasing field at $\Delta H = 2$ T. No spike is found in the measurement with decreasing field. The investigations reveal that the spike is caused by the superheating of the ferromagnetic state due to the magnetocaloric effect when the magnetization data taken on increasing field are used to evaluate the entropy change according to the Maxwell relation as well as the Clausius–Clapeyron equation. Intrinsically, ΔS_{sp} is generated by fictitiously moving the low-temperature part $\Delta S(T, \Delta H)$ and appending it to the plateau around 175 K.

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