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Enhancement of isothermal entropy change due to spin fluctuations in itinerant-electron metamagnetic $La(Fe_{0.88}Si_{0.12})_{13}$ compound

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Abstract

A large isothermal entropy change in $La(Fe_{0.88}Si_{0.12})_{13}$ itinerant-electron metamagnetic (IEM) compound has been investigated by using the Maxwell and Clausius–Clapeyron relations. The entropy change obtained from the Clausius–Clapeyron relation ΔS_m^{CC} gradually decreases with increasing temperature, while that from the Maxwell relation ΔS_m^{Mx} in the magnetic field of 2 T shows a plateau-like behavior in 195–203 K. The difference between ΔS_m^{Mx} and ΔS_m^{CC} is mainly explained by the entropy change in the paramagnetic (P) state below the critical magnetic field of the IEM transition B_C. In the P state, the temperature dependence of susceptibility χ_p is enhanced by spin fluctuations. The thermal variation of $\left|\Delta S_m^{Mx} - \Delta S_m^{CC}\right|$ is well represented by taking that of χ_p as well as B_C into account. Therefore, the plateau-like behavior of ΔS_m^{Mx} comes from the enhancement of the entropy change in the P state, which cancels the decrease of ΔS_m^{CC} due to the decrease of latent heat of the IEM transition with increasing temperature.

Keywords: Magnetocaloric effects; Magnetic entropy change; Itinerant-electron metamagnetic transition; Spin fluctuations

1. Introduction

Recently, we have demonstrated that $La(Fe_xSi_{1-x})_{13}$ compounds exhibit the thermal-induced first-order ferromagnetic (F)–paramagnetic (P) phase transition at the Curie temperature T_C, as well as the itinerant-electron metamagnetic (IEM) transition, that is, a magnetic-field induced P–F phase transition just above T_C [1–4]. The IEM transition exhibits large magnetocaloric effects (MCEs) such as large values of the isothermal entropy change ΔS_m and the adiabatic temperature change ΔT_{ad} [5–10]. The large MCEs of the above compounds attract much attention in the field of both the fundamental research of thermodynamic characteristics of the IEM transition and the practical application of high-performance magnetic refrigerants. For the latter field, the value of T_C has been elevated up to room temperature by hydrogen absorption in $La(Fe_xSi_{1-x})_{13}H_y$ [11,12] and the large MCEs are obtained in the range of 180–330 K, depending on the hydrogen concentration y [7,8,13].

It has been pointed out that the entropy change ΔS_m in $La(Fe_xSi_{1-x})_{13}$ compounds is enhanced by the large latent heat of the IEM transition related to a large magnetization change [7–9]. Furthermore, the IEM transition at finite temperature is closely correlated with the thermal variation of spin fluctuations [14,15]. In itinerant-electron systems, spin fluctuations act as dominant elementally excitations, renormalizing the magnetic free energy[16]. In other words, the thermal variation of spin fluctuations governs the magnetic entropy, especially in the P state. Accordingly, the isothermal magnetic entropy change ΔS_m is also related to spin fluctuations.

In the present study, the thermal variation of ΔS_m related to the IEM transition in $La(Fe_{0.88}Si_{0.12})_{13}$ compound is investigated by using the Maxwell and the Clausius–Clapeyron relations. The obtained results are discussed in terms of the contribution of spin fluctuations to ΔS_m.

2. Experimental

$La(Fe_{0.88}Si_{0.12})_{13}$ compound was prepared by arc-melting in an argon gas atmosphere. To obtain $NaZn_{13}$-type single

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phase, the specimen was annealed in a vacuum quartz tube at 1323 K for 10 days. The magnetization was measured with a superconducting quantum interference device (SQUID) magnetometer. The specific heat measurements were carried out by a relaxation method.

3. Results and discussion

Fig. 1 shows the temperature dependence of the entropy change obtained from the Clausius–Clapeyron relation, ΔS_m^{CC} together with the absolute value of $|\Delta S_m^{Mx}|$ from the Maxwell relation in the magnetic field change from 0 T to $B_{max} = 2$ T for $La(Fe_{0.88}Si_{0.12})_{13}$. From the thermodynamic relation, the Clausius–Clapeyron relation gives the entropy change ΔS_m^{CC} due to the latent heat of the first-order magnetic phase transition as follows:

$$\Delta S_m^{CC} = \Delta M \frac{dB_C}{dT}, \quad (1)$$

where B_C and ΔM are the thermodynamic IEM transition field and the change in magnetization at B_C. As shown in Fig. 1, ΔS_m^{CC} is consistent with the entropy change q/T due to the latent heat q obtained from the specific measurements. Eq. (1) is derived from the condition that the Gibbs energy at $B = B_C$ in the F and the P states equals in magnitude. Therefore, ΔS_m^{CC} is scarcely influenced by the magnetic entropy change in the P state in $B < B_C$ and that in the F state in $B > B_C$. On the other hand, the following equation associated with the Maxwell relation gives the magnetic entropy change in the magnetic field change from 0 to B_{max}:

$$\Delta S_m^{Mx} = \int_0^{B_{max}} \frac{dM}{dT} dB. \quad (2)$$

Therefore, the entropy changes in the P and F states below and above B_C are also involved. Although the behavior of ΔS_m^{Mx} changes with B_{max}, the discussion is dedicated on the data in $B_{max} = 2$ T, because the thermal induced transition above

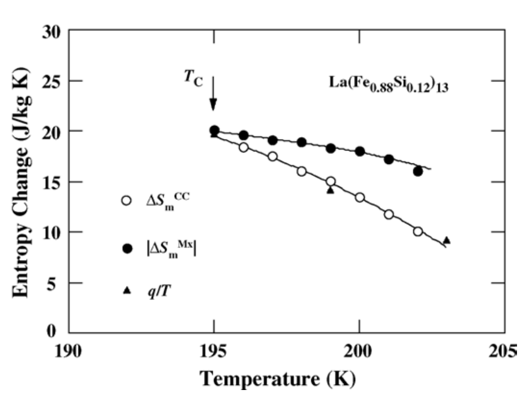

Fig. 1. Temperature dependence of the magnetic entropy change for $La(Fe_{0.88}Si_{0.12})_{13}$ obtained from the Clausius–Clapeyron relation ΔS_m^{CC}, absolute value of that from the Maxwell relation $|\Delta S_m^{Mx}|$ in the magnetic field change from 0 to 2 T, together with the values of latent heat divided by temperature, q/T, obtained from the specific heat data.

2 T becomes relatively broad [7,8], interrupting the precise evaluation of latent heat. Furthermore, from practical view point of magnetic cooling, $B_{max} = 2$ T is approximately the highest value of flux density of high-performance permanent magnets desired to be used in magnetic refrigerators.

It has been revealed that the temperature dependence of B_C is almost proportional to T [7], and hence dB_C/dT of about 0.22 T/K is hardly changed in a temperature range of 195–203 K. On the other hand, ΔM at B_C decreases in a manner as $(\Delta M)^2 \propto T$ [9]. Therefore, the value of ΔS_m^{CC} decreases from 19 J/(kg K) at 195 K to 9 J/(kg K) at 203 K. On the contrary, the temperature dependence of $|\Delta S_m^{Mx}|$ shows a plateau-like behavior around 20–18 J/(kg K) in the temperature range between 195 and 203 K. The difference between ΔS_m^{CC} and $|\Delta S_m^{Mx}|$ becomes larger with increasing temperature, and ΔS_m^{CC} becomes about a half of $|\Delta S_m^{Mx}|$ at 203 K. It is well-known that the first-order phase transition is accompanied by nucleation and growth processes. In increasing magnetic field, the nucleation of the F region does not start just at B_C, but at B_1 which is higher than B_C due to the energy barrier. Furthermore, the IEM transition proceeds within a certain width of magnetic field δ_B above the onset field of the transition B_1 because of growth process of the nucleated F regions in the P matrix. Therefore, Eq. (2) is rewritten as the sum of three terms as follows [17,18]:

$$\Delta S_m = \Delta S^P + \Delta S^{Tr} + \Delta S^F \quad (3)$$

with

$$\Delta S^P = \int_0^{B_1} \frac{\partial M}{\partial T} dB, \qquad \Delta S^{Tr} = \int_{B_1}^{B_2} \frac{\partial M}{\partial T} dB \qquad \text{and}$$

$$\Delta S^F = \int_{B_2}^{B_{max}} \frac{\partial M}{\partial T} dB$$

where B_2 is defined as $B_1 + \delta_B$. The term ΔS^{Tr} in Eq. (3) is related to the IEM transition and should be close to ΔS_m^{CC} when δ_B is small because of differentiability of T and B for the Gibbs energy. Consequently, the difference between $|\Delta S_m^{Mx}|$ and ΔS_m^{CC} is attributed to the rest of terms in Eq. (3) apart from ΔS^{Tr}, i.e., the ΔS^P and ΔS^F denoting the entropy change in the P and F states by applying magnetic field, respectively.

In order to elucidate the relation between $|\Delta S_m^{Mx}|$ and ΔS_m^{CC} described above, the values of ΔS_m^{Mx} at $T = 198$ and 200 K are plotted against B_{max} in Fig. 2. In order to evaluate the values of B_1 and B_2, the fitting of magnetization curves are made in the inset by taking into account the following relation derived from the Landau expansion theory [14].

$$B = a(T)M + b(T)M^3 + c(T)M^5 \quad (4)$$

with

$$a(T) = a(0) + \frac{5}{3}b(0)\xi(T)^2 + \frac{35}{9}c(0)\xi(T)^4,$$

$$b(T) = b(0) + \frac{14}{3}c(0)\xi(T)^2, \qquad c(T) = c(0)$$

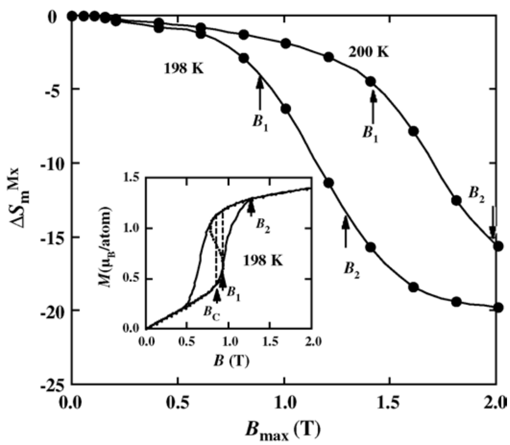

Fig. 2. Magnetic entropy change for $La(Fe_{0.88}Si_{0.12})_{13}$ at 198 and 200 K plotted against the maximum value of magnetic field change B_{max}. The notations B_1 and B_2 are explained in the text. The inset shows the magnetization curve at 198 K. The dotted curve represents the fitting result. Two vertical dashed lines stand for the thermodynamic (B_C) and the onset critical (B_1) fields for the IEM transition.

where $\xi(T)^2$ is the mean square amplitude of spin fluctuations. The IEM transition appears above T_C under the condition of $a(0) > 0$, $b(0) < 0$, $c(0) > 0$ with $3/16 > a(0)b(0)/c(0) > 5/28$. Shown in the inset in Fig. 2 is the magnetization curve at 198 K, together with the fitting result. The value of B_1 is determined from the fitting as the boundary where Eq. (4) changes from the multivalue function to the single-value one. On the other hand, Eq. (4) is given without the nucleation and growth processes, therefore, the value of B_2 is defined experimentally as a closing point of hysteresis above B_1. The ΔS_m^{Mx}–B_{max} curves are nonlinear in analogy with the magnetization curves, and the steepest change is observed between B_1 and B_2. With increasing temperature, the region between 0 to B_1 becomes wider, whereas that between B_2 and B_{max} (=2T) becomes narrower due to the increase of B_C against temperature. It should be noticed that B_2 is larger than 2 T at temperatures above 201 K, therefore, ΔS^F in Eq. (3) has no influence on ΔS_m^{Mx} and the integration region of ΔS^{Tr} given in Eq. (3) is truncated. On the other hand, the value of ΔS_m^{Mx} from 0 to B_1 becomes larger with increasing temperature.

Since no spontaneous magnetic moment exists in the P state, the magnetization M equals to the product of susceptibility χ_p and magnetic field B. Consequently, $\partial M/\partial T$ under the constant magnetic field B in Eq. (2) is dominated by $B(\partial\chi/\partial T)$. It has been discussed that the paramagnetic susceptibility of itinerant electron systems is influenced by the amplitude of thermal spin fluctuations ξ due to the renormalization of free energy by spin fluctuations [14–16].

It is well-known that the temperature dependence of χ_p exhibits a maximum at T_{max} in many IEM compounds[15]. Although χ_p of $La(Fe_xSi_{1-x})_{13}$ compounds decreases continuously against temperature in ambient pressure[4], the maximum phenomenon is observed in χ_p by applying hydrostatic pressure close to the critical value of disappearance in the ferromagnetic ground state [19]. Therefore, it is apparent

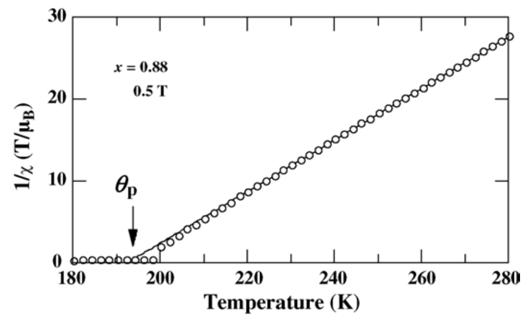

Fig. 3. Temperature dependence of the inverse magnetic susceptibility $1/\chi$ obtained from the thermomagnetization measurement in 0.5 T for $La(Fe_{0.88}Si_{0.12})_{13}$ compound.

that χ_p of the present compound is also dominated by spin fluctuations. To account for the influence of spin fluctuations on χ_p in $La(Fe_{0.88}Si_{0.12})_{13}$, the temperature dependence of inverse magnetic susceptibility $1/\chi_p$ obtained from the thermomagnetization measurement in 0.5 T is plotted in Fig. 3. The temperature dependence of $1/\chi_p$ exhibits a Curie–Weiss like behavior. Therefore, the effective magnetic moment p_{eff} is obtained from the following relation:

$$\chi_p = \frac{C}{(T-\theta_p)} = \frac{\mu_B^2 {p_{eff}}^2}{3k_B(T-\theta_p)} \tag{5}$$

By the least square fitting, p_{eff} is evaluated to be 3.9 μ_B/Fe-atom, being about two times larger than the spontaneous magnetic moment $p_s = 2.0\,\mu_B$/Fe-atom at 4.2 K. Generally, the ratio p_{eff}/p_s becomes almost unity in localized magnetic moment systems because the local amplitude of magnetic moment is independent of temperature [16]. On the other hand, the ratio becomes larger than unity in itinerant electron systems due to thermal variation of amplitude of spin fluctuations [16]. The values of p_{eff}/p_s of itinerant electron ferromagnets are correlated with the Curie temperature. In plots of p_{eff}/p_s against T_C, which is called the Rhodes–Wohlfarth plot; a characteristic increase of p_{eff}/p_s with decreasing T_C towards 0 is common to many kinds of itinerant electron magnets [20,21]. Although the phase transition at T_C of the present compound is of first-order in contrast to conventional ferromagnets exhibiting second-order transitions, the value of p_{eff}/p_s is close to other itinerant-electron magnets with T_C around 200 K.

From Eqs. (3) and (5), the relation between ΔS^P and the Curie constant C is expressed as

$$\Delta S^P = \int_0^{B_1} \left(\frac{B\partial\chi_p}{\partial T}\right)_B \mathrm{d}B = -\frac{C}{2(T-\theta_p)^2}{B_1}^2 \tag{6}$$

Therefore, the enhancement of p_{eff} and C due to spin fluctuations enlarges ΔS^P. Furthermore, it is worth noting that the values of B_1 and B_C show almost the same temperature dependence. As mentioned already, the temperature dependence of B_C has been reported to be proportional to $T - T_C$ [7], and hence, ΔS^P is proportional to $Cg^2(T-T_C)^2/(T-\theta_p)^2$, where g is the coefficient in $B_C = g(T - T_C)$. In Fig. 4, the tempera-

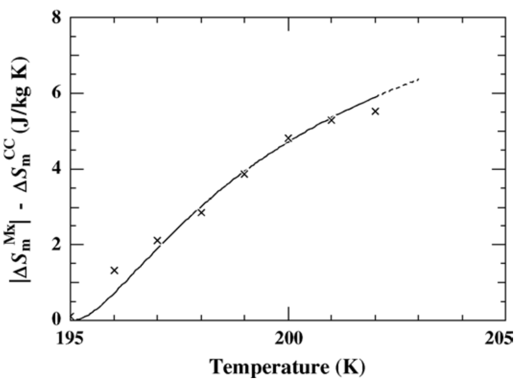

Fig. 4. Thermal variation of difference between the absolute value of the entropy change obtained from the Maxwell relation and the value from the Clausius–Clapeyron relation, $\left|\Delta S_m^{Mx}\right| - \Delta S_m^{CC}$, together with the calculated line from Eq. (6).

ture dependence of $\left|\Delta S_m^{Mx}\right| - \Delta S_m^{CC}$ obtained from Fig. 1 is compared to the numerical evaluation of Eq. (6) by putting the values of $g = 0.22$ T/K, $C = 246$ J K/(kg T^2), $T_C = 195$ K and $\theta_p = 192$ K. The thermal variation of $\left|\Delta S_m^{Mx}\right| - \Delta S_m^{CC}$ is represented by the calculated values of Eq. (6), excepting around 196 K where the contribution of ΔS^F in Eq. (3) makes $\left|\Delta S_m^{Mx}\right| - \Delta S_m^{CC}$ slightly larger than the calculated one. Furthermore, a slight difference between the experimental and the calculated results around 200–203 K arises from a saturated behavior of $\left|\Delta S_m^{Mx}\right| - \Delta S_m^{CC}$ due to the truncated contribution of ΔS^{Tr} associated with the relation $B_1 < B_{max} = 2$ T $< B_2$ at these temperatures. Apart from such slight difference, it is clear that the increase of ΔS^P with temperature mainly cancels the decrease of the latent heat, resulting in the plateau-like behavior of ΔS_m^{Mx} around 196–202 K.

4. Conclusion

Influence of spin fluctuations on the isothermal entropy change ΔS_m has been investigated for $La(Fe_{0.88}Si_{0.12})_{13}$ itinerant-electron metamagnetic (IEM) compound. The entropy change obtained from the Clausius–Clapeyron relation, ΔS_m^{CC}, continuously decreases against temperature above $T_C = 195$ K, while that obtained from the Maxwell relation ΔS_m^{Mx} obtained in the magnetic field change from 0 to $B_{max} = 2$ T exhibits a plateau-like behavior in a temperature range of 196–203 K. Taking the thermal variation of the latent heat and the critical field of the IEM transition into account, the difference between ΔS_m^{CC} and $\left|\Delta S_m^{Mx}\right|$ can be explained by the entropy change in the paramagnetic (P) state, ΔS^P. From the Maxwell relation, the magnitude of ΔS^P below the onset transition field B_1 is related to the thermal variation of paramagnetic susceptibility χ_p. The thermal variation of χ_p shows a Curie–Weiss like behavior with a large Curie constant C due to the thermal variation of spin fluctuations. In consequence, the value of ΔS^P is enhanced by spin fluctuations. By considering the thermal variations of χ_p and the critical field B_C, it is concluded that the thermal increase of ΔS^P cancels the decrease of the latent heat against temperature, resulting in the plateau-like behavior of ΔS_m^{Mx}.

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