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Heat capacity of the $La(Fe_{0.88}Si_{0.12})_{13}$ and $La(Fe_{0.88}Si_{0.12})_{13}H_{1.5}$ compounds with a large magnetocaloric effect

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The heat capacity was investigated in the $La(Fe_{0.88}Si_{0.12})_{13}$ (the Curie temperature $T_C = 194$ K) and $La(Fe_{0.88}Si_{0.12})_{13}H_{1.5}$ ($T_C = 334$ K) compounds at the temperatures between 1.8 and 350 K. The coefficient of γ of the low-temperature specific heat $C_p(T) = \gamma T + \beta T^3$ changes from 9.4 mJ/(g atom K^2) to 6.4 mJ/(g atom K^2) for $La(Fe_{0.88}Si_{0.12})_{13}$ and $La(Fe_{0.88}Si_{0.12})_{13}H_{1.5}$, respectively. The heat capacity was measured at various magnetic fields in the vicinity of T_C for the $La(Fe_{0.88}Si_{0.12})_{13}$ compound. It was found that the heat capacity in the magnetic field exceeds the heat capacity in zero magnetic field around T_C. It is proposed that the enhancement of the anomaly of the heat capacity is caused by the work of the elastic forces to form a elastic stress by the magnetizing. The maximum of the magnetocaloric effect takes place in a paramagnetic state near T_C where the metamagnetic phase transition occurs.

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I. INTRODUCTION

Recently, a remarkable result concerning materials for magnetic refrigerators has been reported: the $La(Fe_{0.88}Si_{0.12})_{13}$ compound exhibits large magnetocaloric effect (MCE) in relatively low magnetic fields 0–20 kOe around the Curie temperature $T_C = 194$ K and the T_C can be increased up to 336 K due to hydrogen absorption.[1–5] Therefore the $La(Fe_{0.88}Si_{0.12})_{13}$ and $La(Fe_{0.88}Si_{0.12})_{13}H_{1.5}$ compounds are the best candidates for magnetic refrigerants. Above T_C the itinerant-electron metamagnetic (IEM) transition from the paramagnetic (PM) to the ferromagnetic (FM) state is observed when applying a magnetic field in a few kiloOersteds. It means that the T_C increases with the magnetic field.[1] This IEM transition is accompanied by a large volume magnetostriction of about 1.5% at the temperature $T = 200$ K.[6] The MCE for the $La(Fe_{0.88}Si_{0.12})_{13}$ is found to be about 0.3 K/kOe from the direct measurements[4] and about 0.4 K/kOe from indirect measurements[1] just above T_C. The $La(Fe_{0.88}Si_{0.12})_{13}$ compound has a cubic structure $NaZn_{13}$ ($D2$) with space group $Fm3c$ (O_h). As shown by x-ray diffraction experiments the volume change of about $\Delta V/V \sim 1.2\%$ caused by the IEM transition is isotropic in the present compound.[6–8] Under external pressure the Curie temperature T_C decreases down to 80 K at 1 GPa.[9] The volume change in the external magnetic fields is in good agreement with the spontaneous volume change at the transition through the T_C.[6,10] The electron band structure calculation gives some basis for a description of the mechanism of the transition within the framework of the theory of the itinerant-electron metamagnetism with significant spin fluctuations.[10] For the first time the heat capacity data were obtained in zero and several values of magnetic fields: 10, 20, 30, and 50 kOe for these compounds in order to calculate an adiabatic change of temperature ΔT_{ad}.[1] In the present paper we studied the low-temperature heat capacity of the $La(Fe_{0.88}Si_{0.12})_{13}$ and $La(Fe_{0.88}Si_{0.12})_{13}H_{1.5}$ to obtain the values of the electron density of states (DOS) at the Fermi level. Moreover we measured the heat capacity around T_C in the zero and nonzero magnetic fields to examine the large values of the MCE in $La(Fe_{0.88}Si_{0.12})_{13}$. On the way of the research the phenomenon was found, namely, the heat capacity increased in the external magnetic field around T_C. This phenomenon will be discussed below.

II. EXPERIMENTAL DETAILS

The $La(Fe_{0.88}Si_{0.12})_{13}$ compound was prepared by arc melting in an Ar gas atmosphere. The purities of the three starting elements were all better than 99.9%. The heat treatment for a homogenization was carried out in a vacuum quarts tube at 1323 K for 12 days with subsequent quenching in a water. The single phase with the $NaZn_{13}$-type structure was confirmed by x-ray powder diffraction. Annealing in hydrogen gas atmosphere at 103 MPa and 500 K was performed for hydrogen absorption by the compound. The heat capacity, the magnetization, ac susceptibility were measured using PPMS-9 and MPMS-5XL devices (Quantum Design) in magnetic fields up to 90 kOe at the Cryomagnetic Center of the Institute of Metal Physics.

The heat capacity in zero magnetic fields and in various magnetic fields was measured on PPMS-9 without remounting of the specimen. To receive the heat capacity temperature dependence in detail and to bypass the known difficulties of the measurement of the heat capacity at the first order phase transition,[11] we performed the measurements in a fixed external magnetic field a few times using the same program, each time changing the start temperature on the 0.1 K. With the result that well reproduced specific heat data was received in the fixed magnetic field at the PM-FM phase transition.

III. EXPERIMENTAL RESULTS

The temperature dependence of the heat capacity for the $La(Fe_{0.88}Si_{0.12})_{13}$ and the $La(Fe_{0.88}Si_{0.12})_{13}H_{1.5}$ compounds in zero external magnetic fields is given in Fig. 1. Obviously the λ-type peaks of the heat capacity are caused by PM-FM phase transitions. The T_C changes from 194 K to 334 K for the compound due to the hydrogen absorption. This fact is in

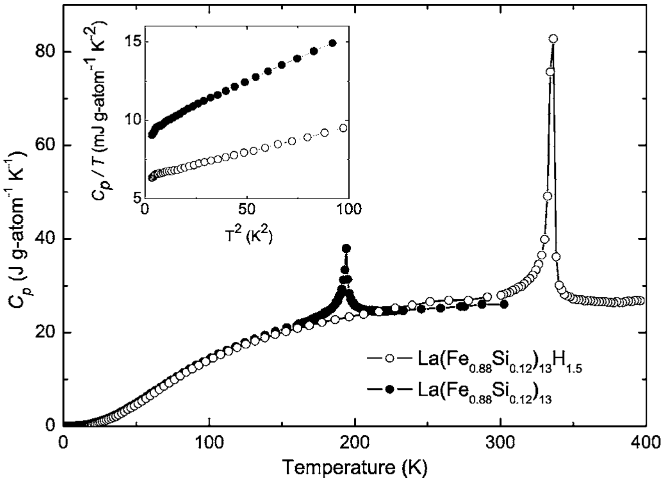

FIG. 1. Temperature dependencies of the heat capacity C_p for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ and La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ in zero magnetic field. The inset shows dependence of C_p/T versus T^2.

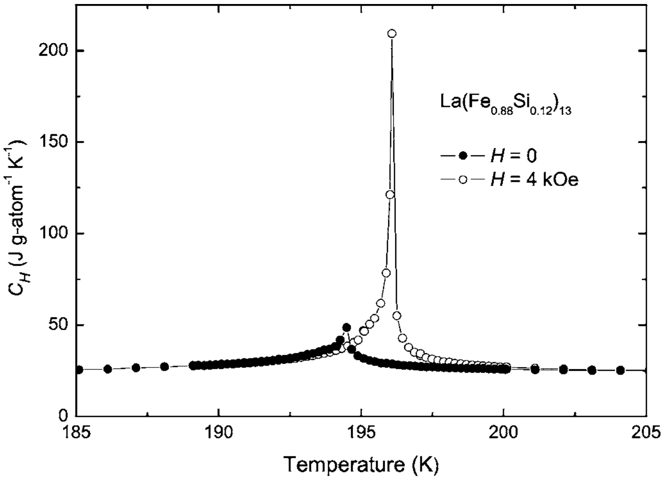

FIG. 3. Temperature dependencies of the heat capacity C_H in zero external magnetic field and in the external magnetic field $H = H_D = DM_S$ for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$.

a good agreement with the results of magnetic and heat capacity measurements.[1] The observed peak of the heat capacity of the hydride is wider and is higher in magnitude than for the compound without hydrogen. The low-temperature behavior of the heat capacity of the compounds may be described as $C/T = \gamma + \beta T^2$. It is illustrated in the inset of Fig. 1, where $\gamma = 9.4$ mJ/(g atom K) for the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ and $\gamma = 6.4$ mJ/(g atom K) for the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_{1.5}$. It means that the DOS at the Fermi level $g(E_F) = 3\gamma/(\pi^2 N_A k_B^2)$ changes from 4.0 to 2.7 states/(eV atom), respectively. Figure 2 shows the temperature dependencies of the heat capacity in various low magnetic fields H and in zero magnetic field. The heat capacity peak (anomaly) near T_C becomes higher and wider with increasing of the magnetic field. At some magnetic field $H_D \approx 4$ kOe the peak achieves the maximum value (Fig. 3). At the further increase of the magnetic field, the peak widens and decreases. Figure 4 shows the heat capacity in zero magnetic field and in the magnetic field 20 kOe. Figure 5 summarizes the temperature dependencies of the heat capacity in various external magnetic fields. One can see in Figs. 2–5, the peak of the heat capacity in the nonzero external magnetic fields exceeds the peak of the heat capacity in zero magnetic field considerably. The T_C increases up to 207 K with increasing the magnetic field up to 30 kOe.

To understand the primary cause of the increase of the heat capacity in low magnetic fields around T_C we measured the magnetic properties of the same specimens of these compounds. In Fig. 6, the magnetization curves are shown at the various temperatures for both FM and PM states. The critical field of the IEM transition H_C was defined as a inflection point on the magnetization curves. The H_C is equal 20 kOe at $T = 205$ K, and $H_C \approx 70$ kOe at $T = 230$ K in La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$. It should be noted that the IEM transition

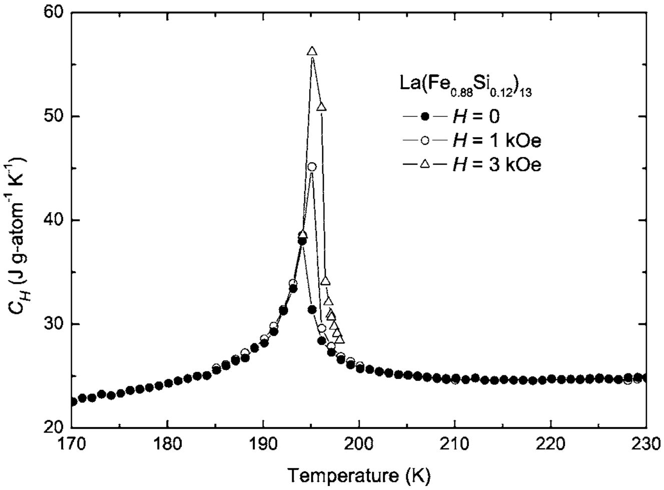

FIG. 2. Temperature dependences of the heat capacity C_H in zero external magnetic field and in low external magnetic fields $H < H_D = DM_S$, but in the zero internal magnetic field $H_i = 0$ for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$.

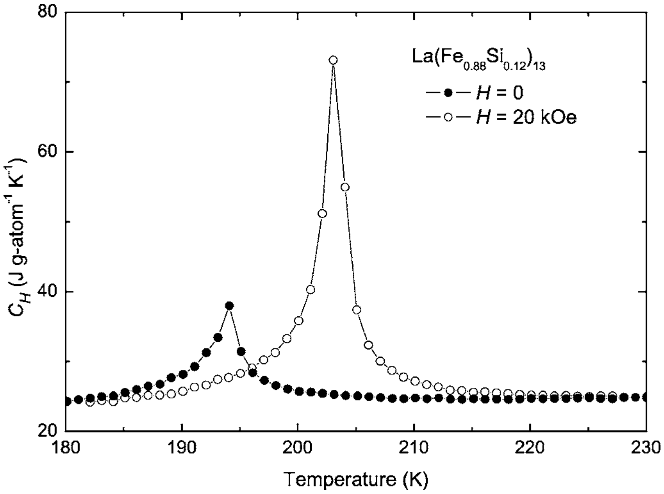

FIG. 4. Temperature dependences of the heat capacity C_H in zero external magnetic field and in the external magnetic fields $H > H_D = DM_S$, i.e., in the internal nonzero magnetic fields $H_i > 0$ for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$.

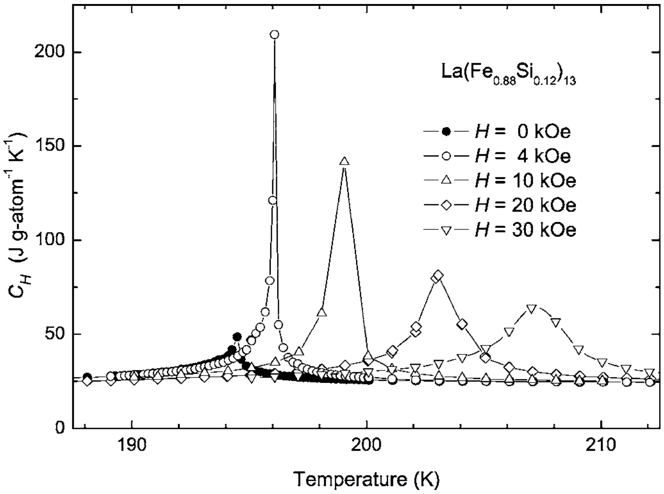

FIG. 5. Temperature dependencies of the heat capacity C_H in various internal magnetic fields H_i in the external magnetic fields $H=0,4,10,20,30$ kOe for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$.

is observed at the temperature which is far away $T_C = 194$ K (at $H=0$). Our measurements of the magnetization curve in pulse magnetic fields for the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ show that the H_C is about 160 kOe at $T=273$ K. The magnetization curves have a large hysteresis of the IEM transition, as shown in Fig. 6, where arrows show direction of the change of the magnetic field. Figure 7 shows the magnetization curves of the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_{1.5}$ at the various temperatures for both FM and PM states. The H_C is about 10 kOe at $T=340$ K. We performed magnetic measurements on the sphere form specimens. Therefore the initial slope of magnetization curves is determined by the demagnetizing factor of the ball at $T<T_C$. It was known, that these compounds have extremely small coercive force, that is a small magnetic anisotropy and we confirm it by our measurements of the hysteresis loop. The magnetization depending on the temperature is shown in Figs. 8 and 9 for the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ and for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_{1.5}$, respectively.

Figures 8 and 9 show that the temperature dependencies of the magnetization are constants in low magnetic fields at $T<T_C$. It arises from a demagnetizing field of the specimen with the demagnetizing factor D. In this case the magnetic field inside the specimen H_i is equal to zero,

$$H_i = H - DM, \tag{1}$$

where M is the magnetization. Therefore the magnetization (M) is proportional to the applied field $M=H/D$ and M does not depend on the temperature at $T<T_C$ in the low external magnetic fields. The resultant magnetic field inside the specimen begins to increase when $H>H_D=DM_S$, where M_S is temperature-dependent spontaneous magnetization and H_D is the demagnetizing field, in our case $H_D \approx 4$ kOe (see Figs. 6 and 7).

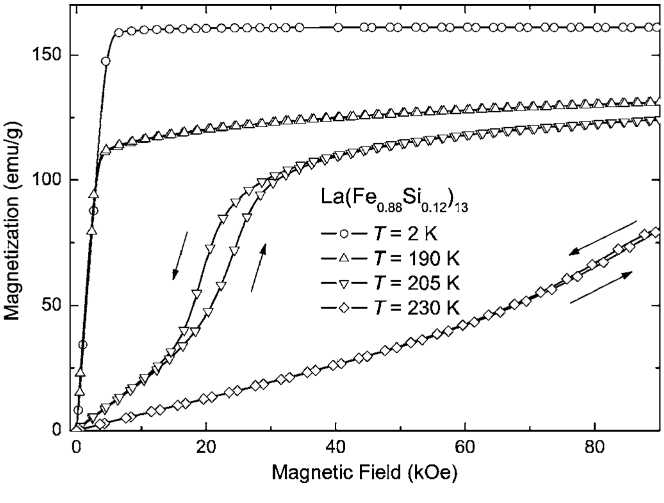

FIG. 6. Magnetization curves at different temperatures for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ ($T_C=194$ K in zero external magnetic field).

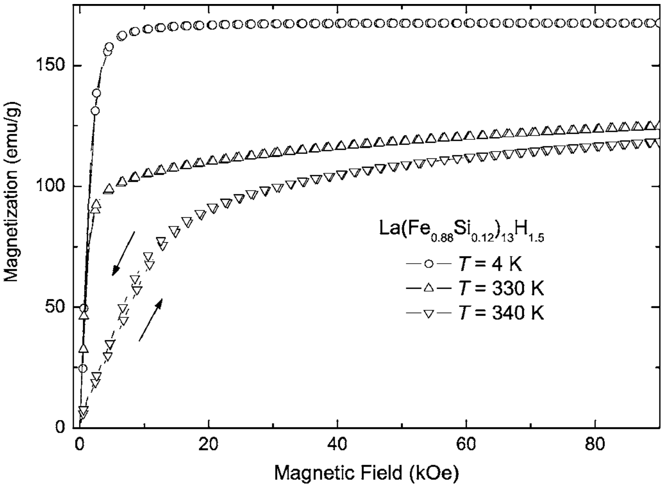

FIG. 7. Magnetization curves at different temperatures for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_{1.5}$ ($T_C=334$ K in zero external magnetic field).

IV. DISCUSSION

The low-temperature heat capacity of these compounds is described as $C/T=\gamma+\beta T^2$, where $\gamma=9.4$ mJ/(g atom K) for

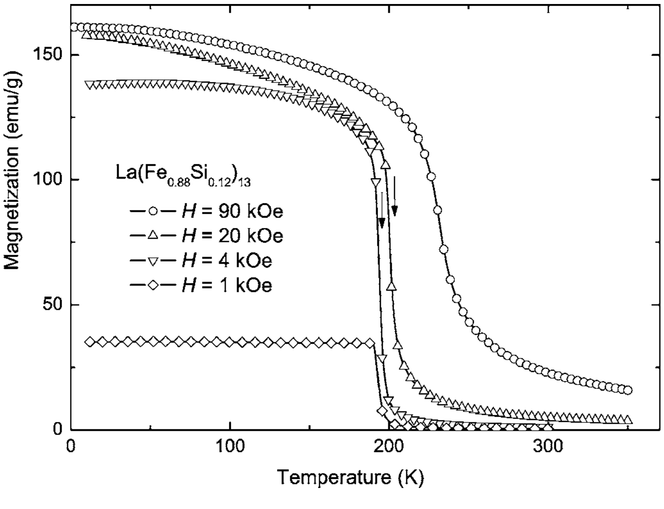

FIG. 8. Temperature dependencies of the magnetization in various external magnetic fields for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$. The temperatures of the heat capacity maximum are marked by arrows.

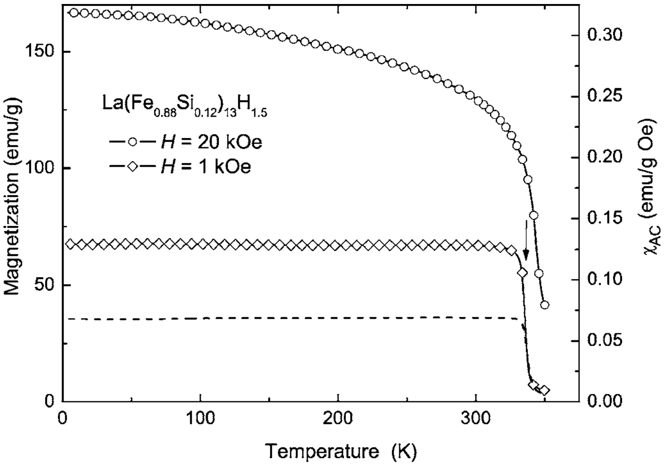

FIG. 9. Temperature dependencies of the magnetization in various external magnetic fields for $La(Fe_{0.88}Si_{0.12})_{13}H_{1.5}$. The temperature of the heat capacity maximum is marked by the arrow. The dashed line shows the temperature dependence of the ac susceptibility χ_{AC} (on the right-hand scale).

the $La(Fe_{0.88}Si_{0.12})_{13}$ and $\gamma = 6.4$ mJ/(g atom K) for the $La(Fe_{0.88}Si_{0.12})_{13}H_{1.5}$. Because of the hydrogenation the DOS changes from 4.0 to 2.7 states/(eV atom) and the Debye temperature changes from 317 K to 392 K we estimated from γ and β. The band model of the IEM transition contradicts obtained decreasing of the DOS because of the hydrogenation. The band mechanism supposes that in magnetic fields the DOS increases in its value up to Stoner's critical value for a start of the ferromagnetism. However, on the one hand, the Curie temperature and the lattice parameter considerably increase because of both the hydrogenation and the external magnetic fields. On the other hand, the DOS decreases because of the hydrogenation. From these facts we presuppose that the DOS will decrease in external magnetic fields too. The T_C increases owing to the large change of the lattice parameters because of both the hydrogenation and the external magnetic fields. The rise of the lattice parameters stimulates presumably of the decrease of the DOS instead of its increase. The IEM transition happens due to the strong dependence of the exchange interaction on the lattice parameter (on the interatomic distance) and it is induced by the magnetostriction deformations at the magnetization process, as was discussed for $La(Fe_{0.873}Co_{0.007}Al_{0.12})_{13}$.[12]

Magnetic phase transitions FM – PM in external magnetic fields near the critical point (near T_C) were widely discussed in the past 60 years.[13–18] The difference between the heat capacity in zero and nonzero external magnetic fields has been found. In low external magnetic field the phase transition is realized from the uniformly magnetized paramagnetic state to the nonuniformly magnetized ferromagnetic state: UPM-NFM. In high external magnetic fields the transition is realized from the uniformly magnetized paramagnetic state to the uniformly magnetized ferromagnetic state: UPM-UFM. The singular behavior of the specific heat and the resistivity was observed for the EuS (Refs. 13,16,17) and for the gadolinium[18] in the nonzero field near their Curie points. These singularities were called "kink points." These "kink phenomena" were observed in the case that the T_C did not increase in the external magnetic field. We observed the "kink phenomenon" in the case of the rise of the T_C in external magnetic fields for the $La(Fe_{0.88}Si_{0.12})_{13}$ compound.

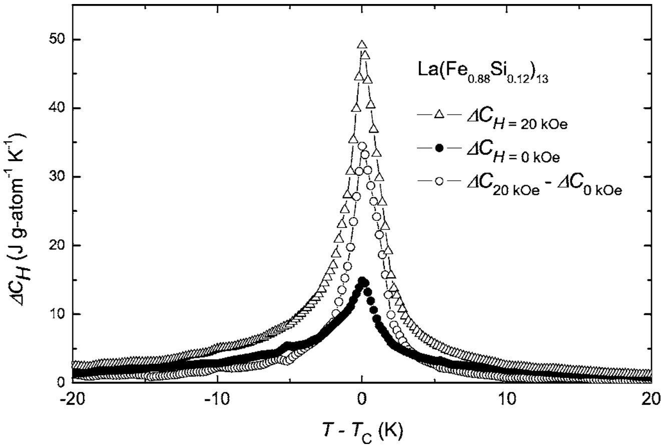

FIG. 10. Temperature dependencies of the excess heat capacity ΔC_H in the scale of the "T-T_C" in zero field and nonzero magnetic field ($H = 20$ kOe) for $La(Fe_{0.88}Si_{0.12})_{13}$. The difference between these curves ΔC_{20}-ΔC_0 is also shown.

For the $La(Fe_{0.88}Si_{0.12})_{13}$ we found that in comparison with the heat capacity in zero external magnetic fields the increase of the heat capacity near T_C in nonzero external magnetic fields is caused by a changing of the total energy at the magnetization process of the specimen. In other words, the elastic energy, the magnetoelastic energy, and the magnetostatic energy of the specimen change when external magnetic field applies. The additional energy is equal to the work of deformation, which can be done to form the magnetized state (NFM or UFM) of the specimen in the external magnetic field. The conditions minimizing the total energy of the specimen determine a part of each component of the energy. The ratio between these parts depends on elastic, magnetoelastic constants, the demagnetizing factor, and the temperature range. The critical field of the IEM transition is equal to zero at T_C. At the low magnetic fields the phase transition from uniformly magnetized PM state (UPM) to nonuniformly magnetized FM state (UPM-NFM) takes place. When the external magnetic field is at the high value of the demagnetizing field, the specimen is uniformly magnetized ferromagnetic (UFM). In the high external magnetic field the phase transition from uniformly magnetized PM state (UPM) to uniformly magnetized FM state (UPM-UFM) takes place. The heat capacity is the temperature derivative of the total energy and reflects the change of the elastic and magnetoelastic components of the total energy too. Figures 2 and 3 show the temperature dependencies of the heat capacity at the UPM-NFM transitions. Figures 4 and 5 show the temperature dependencies of the heat capacity at the UPM-UFM transitions.

Figure 10 shows the temperature dependencies of the anomaly of the heat capacity $\Delta C_H(T)$ versus $T - T_C$ which were measured in zero and nonzero external magnetic field ($H = 20$ kOe). To define ΔC_H we used the Debye function for the regular (lattice) part of the heat capacity. The difference between these dependencies in Fig. 10 gives the heat capacity increase which is caused by the external magnetic field. The additional energy of the magnetic phase transition is equal,

$$\Delta E_H = \int_{T_1=170\ \mathrm{K}}^{T_2=230\ \mathrm{K}} \Delta C_H(T,H)dT \quad (H=\mathrm{const}). \tag{2}$$

Substitution in Eq. (2), using data from Fig. 10, gives $\Delta E_{20} = 264.4$ J/g atom at $H=20$ kOe, and $\Delta E_0 = 111.7$ J/g atom at $H=0$. The ratio between them is equal to

$$\Delta E_{20}/\Delta E_0 = 2.37. \tag{3}$$

Below we will discuss the origin of the additional energy ΔE_H at the magnetic phase transition on basis of Néel's theory, which is well described in textbook Chikazumi,[19] and we will use the same notation. The elongation of diameter of the ferromagnetic sphere along a direction which makes an angle φ with direction of magnetization is given by $\delta l/l = e\cos^2\varphi$, that is in saturated state $(\delta l/l)_{\mathrm{sat}} = e$. When the domain magnetizations are distributed at random in a demagnetized state the average deformation is given by the average from $\varphi=0$ to $\varphi=\pi/2$, thus $(\delta l/l)_{\mathrm{demag}} = e/3$. Hence, the saturation magnetostriction is given by

$$(\delta l/l)_{\mathrm{sat}} - (\delta l/l)_{\mathrm{demag}} = 2e/3. \tag{4}$$

In the magnetic dipole pair model when the distance between the atomic magnetic moments is variable, the pair interaction energy is expressed as

$$w(r,\varphi) = g(r) + l(r_0)\left(\cos^2\varphi - \tfrac{1}{3}\right), \tag{5}$$

where r is the interatomic distance. The first term, $g(r)$, is the exchange interaction term; it is independent of the direction of magnetization. Thus the crystal deformation caused by the first term does not contribute to the usual magnetostriction, but it does play an important role in the volume magnetostriction. The second term represents the dipole-dipole interaction, which depends on the direction of magnetization, and can be the main origin of the usual magnetostriction.

The energy in terms of lattice strain and direction of domain magnetization is called the magnetoelastic energy E_{magel}. In a unit volume of a simple cubic lattice we have

$$\begin{aligned} E_{\mathrm{magel}} = {} & B_1\left[e_{xx}\left(\alpha_1^2 - \tfrac{1}{2}\right) + e_{yy}\left(\alpha_2^2 - \tfrac{1}{2}\right) + e_{zz}\left(\alpha_3^2 - \tfrac{1}{2}\right)\right] \\ & + B_2(e_{xy}\alpha_1\alpha_2 + e_{yz}\alpha_2\alpha_3 + e_{zx}\alpha_3\alpha_1), \end{aligned} \tag{6}$$

where

$$B_1 = N\left(\frac{\partial l}{\partial r}\right)r_0, \quad B_2 = 2Nl,$$

N is the number of magnetic atoms per unit volume, $e_{xx}, e_{yy}, e_{zz}, e_{xy}, e_{yz}, e_{zx}$ are strain tensor components, $\alpha_1, \alpha_2, \alpha_3$ are the direction cosines of domain magnetization. For bcc and fcc lattices the expression will be the same with other B_1 and B_2. Hence the magnetoelastic energy is a linear function with respect to $e_{xx}, e_{yy}, \ldots, e_{zx}$. The elastic energy is given by

$$\begin{aligned} E_{\mathrm{el}} = {} & \tfrac{1}{2}c_{11}(e_{xx}^2 + e_{yy}^2 + e_{zz}^2) + \tfrac{1}{2}c_{44}(e_{xy}^2 + e_{yz}^2 + e_{zx}^2) \\ & + c_{12}(e_{yy}e_{zz} + e_{yy}e_{xx} + e_{zz}e_{xx}), \end{aligned} \tag{7}$$

where c_{11}, c_{44}, and c_{12} are the elastic modules. The elastic energy is a quadratic function of the strain of the crystal.

In the first approximation, a rotation of the magnetization does not give rise to any volume magnetostriction.[19] It must be remarked, that the volume of the specimen had already been changed when the ferromagnetism was generated because of the first term of Eq. (5). For the simple cubic lattice the energy of crystal is changed by lattice strain by the amount

$$E_{\mathrm{volmag}} = N\left(\frac{\partial g}{\partial r}\right)r_0(e_{xx} + e_{yy} + e_{zz}). \tag{8}$$

It should be noted that the shape of the specimen (the form effect) gives rise not only to volume magnetostriction but also to ordinary magnetostriction. For an ellipsoid of rotation with dimensional ratio $k = l/d$, where l and d denote the length and width of the ellipsoid, the demagnetizing factor D, expressed as a function of strain, is

$$D = D_0 + \frac{dD}{dk}\left(\frac{\partial k}{\partial e_{xx}}e_{xx} + \frac{\partial k}{\partial e_{yy}}e_{yy} + \frac{\partial k}{\partial e_{zz}}e_{zz}\right).$$

For an elongated ellipsoid of rotation, we have

$$D = D_0\left\{1 - a\left[e_{xx} - \tfrac{1}{2}(e_{yy} + e_{zz})\right]\right\},$$

where

$$a = \frac{2\ln 2k - 3}{\ln 2k - 1}.$$

Then the magnetostatic energy of the system can be given by

$$E_D = \tfrac{1}{2}DM^2 = \tfrac{1}{2}M^2D_0\left\{1 - a\left[e_{xx} - \tfrac{1}{2}(e_{yy} + e_{zz})\right]\right\}. \tag{9}$$

The resultant strain can be determined by minimizing the total energy

$$\Delta E = E_{\mathrm{magel}} + E_{\mathrm{el}} + E_{\mathrm{volmag}} + E_D. \tag{10}$$

It is given by

$$e_{xx} = \frac{1}{2}\frac{aD_0M^2}{c_{11} - c_{12}}, \quad e_{yy} = e_{zz} = -\frac{1}{4}\frac{aD_0M^2}{c_{11} - c_{12}}. \tag{11}$$

To summarize these effects, the magnetovolume energy is a linear function of the strain of the crystal and the magnetostatic energy is a quadratic function of the strain of the crystal if we assume that $\delta l/l \sim (M/M_S)^2$. Therefore the ratio of the demagnetizating state energy ($\Delta E_{\mathrm{demag}}$) to the saturated state energy (ΔE_{sat}) will be determined by the ratio of these components, $E_{\mathrm{magel}}, E_{\mathrm{el}}, E_{\mathrm{volmag}}, E_D$ in the total energy at the PM-FM phase transition. In our case we may suppose that $\Delta E_{\mathrm{sat}}/\Delta E_{\mathrm{demag}} = \Delta E_{20}/\Delta E_0$.

Let the strain be $(\delta l/l)_{\mathrm{demag}} = (1/3)e$ in the zero external magnetic field, and $(\delta l/l)_{\mathrm{sat}} - (\delta l/l)_{\mathrm{demag}} = (2/3)e$ in the high external magnetic field. For the first case when E_{magel} and E_{volmag} are the essential parts in the total energy, the ratio gives

$$\frac{\Delta E_{20}}{\Delta E_0} = \frac{(\delta l/l)_{\mathrm{sat}} - (\delta l/l)_{\mathrm{demag}}}{(\delta l/l)_{\mathrm{demag}}} = \frac{(2/3)}{(1/3)} = 2. \qquad (12)$$

The second case when E_{el} and E_D are the essential parts in the total energy the ratio is

$$\frac{\Delta E_{20}}{\Delta E_0} = \frac{[(\delta l/l)_{\mathrm{sat}} - (\delta l/l)_{\mathrm{demag}}]^2}{(\delta l/l)^2_{\mathrm{demag}}} = \frac{(2/3)^2}{(1/3)^2} = 4. \qquad (13)$$

In our case from the heat capacity data in Fig. 10 this ratio is equal to 2.37 as calculated from Eq. (3). That means the magnetoelastic and magnetovolume energies together with elastic and magnetostatic energies are essential in balance of the total energy at this magnetic phase transition. The anomaly of the heat capacity near T_C shows the derivative with respect to temperature of this additional energy at the magnetic phase transition,

$$\Delta C_H(T) = d(\Delta E_H)/dT. \qquad (14)$$

In comparison with the heat capacity in zero external magnetic fields it was found that the magnetoelastic, magnetovolume, elastic and magnetostatic components in the heat capacity are too large in nonzero magnetic field at the PM-FM phase transition. We are forced to conclude that the additional heat capacity consists in the main of these listed components of energy at the magnetic phase transition in zero magnetic fields too. In zero external magnetic fields the additional heat capacity (called "the magnetic heat capacity") will be determined by the same components of the energy for the spontaneously deformed state, which is caused by the spontaneous magnetization.

The amount of the magnetic entropy may be defined by the expression

$$S_{\mathrm{ad}} = \int_0^{T>T_C} \frac{\Delta C_H(T)}{T} dT = \int_0^T \frac{1}{T} \frac{d(\Delta E)}{dT} dT. \qquad (15)$$

The temperature dependences of the additional entropy are calculated from the data of Figs. 2–5 for various external magnetic fields, using Eq. (15), and are shown in Fig. 11. We found that the magnetoelastic and magnetovolume parts of the total energy play the essential role in the change of the entropy. Moreover the elastic and magnetostatic parts of the energy give quite noticeable contributions to the entropy. Since Debye's work,[20] where he has proposed to use an adiabatic demagnetizing to reach a low temperature, it is traditionally neglected of the change of the elastic state of the lattice: volume of the rigid body is saved, the elastic energy at the magnetization process is not changed, the magnetoelastic and magnetostatic energies are not considered.[21] The approximation consists of that the magnetocaloric effect in solids is the result of the entropy variation due to the coupling of a magnetic spin system with magnetic field. But the total entropy S of a magnetic solid is the sum of the electronic, lattice, and magnetic entropies S_E, S_L, and S_M, respectively. Among the three, the magnetic entropy strongly depends on the magnetic field, while usually the electronic and the lattice entropies are practically magnetic-field independent. Both S_E and S_L remain constant when the magnetic entropy decreases on ΔS_M at the constant temperature.[22,23] In this conventional consideration, the adiabatic process from one entropy curve for a zero external magnetic field to another for a nonzero external magnetic field gives the value of the adiabatic change of the temperature of the specimen,

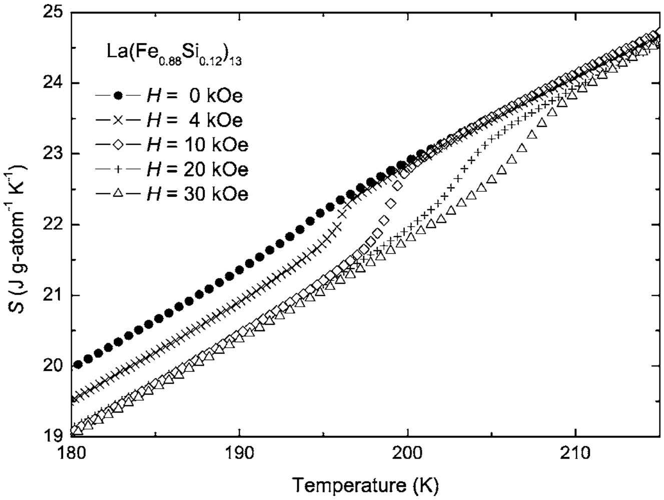

FIG. 11. Temperature dependences of the total entropy in various external magnetic fields for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$.

$$\Delta T_{\mathrm{ad}}(T)_{\Delta H} = [T(S)_{H_2} - T(S)_{H_1}]_S. \qquad (16)$$

However we conclude that the magnetoelastic and elastic entropies change significantly both with the temperature and with the external magnetic field owing to the magnetization process. It means that in low external magnetic fields the magnetization process comes with the change of the entropy, that is to say the magnetization process is not isentropic process. The increase of the external magnetic field up to the value of the demagnetizing field of the specimen is accompanied by a reversible change of the magnetoelastic and elastic entropies without a variation of the temperature, i.e., this process will be isothermal. When the increase of the external magnetic field cannot be compensated further due to the demagnetizing field of the specimen then the specimen becomes the uniformly magnetized ferromagnet. Starting with this magnetic field the magnetoelastic and elastic entropies will not change and the magnetization process will be close to the isentropic process and as a result the temperature of the specimen will change.

Therefore to calculate the $\Delta T_{\mathrm{ad}}(T)$ precisely it is necessary to use two entropy curves, which are appropriate to the change of the internal magnetic fields inside the specimen. In our case the external magnetic field existed inside the specimen in the magnetic fields above $H \geq H_D \simeq 4$ kOe. Therefore when the external magnetic field changes from 0 to 20 kOe, we may estimate that the internal magnetic field changes about $\Delta H \approx H_2 - H_1 = 20 - 10 = 10$ kOe. In a Fig. 12 the curve of the adiabatic temperature change is obtained from the data of the entropy between the external magnetic fields $H_2 = 20$ kOe and $H_1 = 10$ kOe. The maximum value of $\Delta T_{\mathrm{ad}}(T) \cong 3.5$ K/10 kOe is the same as the experimentally observed value[3] and it lies above the T_C.

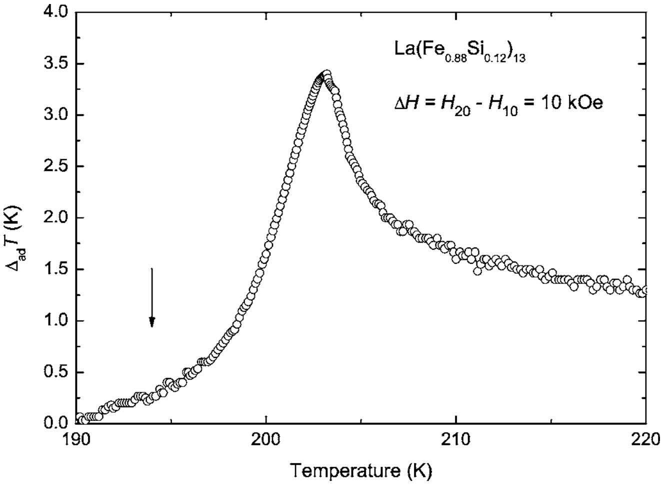

FIG. 12. Temperature dependence of the adiabatic temperature change T_{ad} resulting from the magnetic field variation from 10 to 20 kOe. The Curie temperature in zero magnetic field (T_C =194 K) is marked by the arrow.

V. CONCLUSION

As a result of the heat capacity measurements it was found that the density of states at the Fermi level $g(E_F)$ changes under hydrogenation from 4.0 states/(eV atom) for the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ to 2.7 states/(eV atom) for the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_{1.5}$. The DOS decrease conflicts with the model of the itinerant-electron metamagnetic phase transition. Indeed, for the realization of the IEM phase transition it is necessary to increase the DOS up to Stoner's critical value. Really the T_C and the lattice parameter increase both at the hydrogenation and at the external magnetic field increase for the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$. At the same time the DOS decreases under hydrogenation and we believe that the DOS decreases in the external magnetic fields too.

It was shown that the heat capacity in the magnetic field surpasses the heat capacity in zero magnetic field around T_C for the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ compound. We believe that the heat capacity in the external magnetic fields increases the value of the work for the change of the magnetoelastic, elastic, magnetovolume, and magnetostatic energies at the forming of the magnetized state of the specimen. This result is the first experimental evidence of the heat capacity dependence on the elastic constants and on the shape of the specimen at the magnetic phase transition from PM to FM state.

The heat capacity increases in small external magnetic fields (less than the demagnetizing field in FM state). It means that the elastic part of the entropy changes at the spontaneous magnetic phase transition in the small fields when the demagnetizing field of the specimen compensates the external magnetic field inside it. Hence, the magnetization process in small magnetic fields goes with the change of the elastic part of the entropy at the constant temperature. In other words, the magnetocaloric effect is absent in small magnetic fields. The maximum of the MCE is observed in the PM range when $T \geq T_C$, owing to the metamagnetic phase transition, that is caused by the change of the elastic state under the large magnetostriction deformation in the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$.

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