Itinerant-electron metamagnetic transition and large magnetovolume effects in La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds

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Magnetic properties and magnetovolume effects have been investigated for itinerant-electron metamagnetic La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds. At the Curie temperature T_{C1}, a first-order magnetic phase transition takes place in the concentration range $0.86 \leq x \leq 0.88$. With increasing Fe concentration, the Curie temperature decreases and the critical temperature of the itinerant-electron metamagnetic (IEM) transition increases, accompanied by a more sharp IEM transition. For the compound with $x = 0.88$, a large volume change of about 1% follows the thermal induced transition at T_{C1}. The value of T_{C1} is significantly decreased by applying hydrostatic pressure, whereas the pressure dependence of the spontaneous magnetization is relatively small. These results are explained by the negative mode-mode coupling among spin fluctuations.

I. INTRODUCTION

The itinerant-electron metamagnetic (IEM) transition, that is, the first-order transition from the Pauli paramagnetic to the itinerant-electron ferromagnetic state, has been extensively investigated from both the experimental and theoretical viewpoints.[1–13] Wohlfarth and Rhodes initially discussed the IEM transition by using a Landau-type expansion up to fourth power of the uniform magnetization.[9] Shimizu also discussed the IEM transition by considering up to the sixth power term.[10] It is important to note that this transition involves the influence of spin fluctuations as well as the magnetovolume effects at finite temperatures.[6,8,12,13]

The IEM transition is characterized by two quasidegenerated states of itinerant electrons.[9–12] It should be noticed that the quasidegenerated magnetic states has also been discussed in connection with Invar anomalies, namely, extremely large magnetovolume effects, in Fe-based alloys such as Fe-Ni and Fe-Pt systems.[14] In the past, the IEM transition and the magnetovolume effect were independently discussed. However, recent theoretical studies disclose the close relation between these phenomena.[13]

Experimental results on the IEM transition have so far been restricted to Co-based Laves phase[1–6] and pyrite compounds,[7,8] except for MnSi which exhibits an IEM transition under high pressures.[15] Recently, we have demonstrated that La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds exhibit a first-order magnetic phase transition at the Curie temperature T_{C1}, as well as an IEM transition above T_{C1}.[16] It should be emphasized that Fe-based itinerant-electron metamagnetic compounds have been found for the first time. The most striking characteristic of La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds is that the magnetic moment induced by the IEM transition exceeds $1 \mu_B$ just above T_{C1}, accompanied by a large volume change. In addition, marked magnetovolume effects have been reported for isostructural La(Fe$_x$Al$_{1-x}$)$_{13}$ compounds.[17] Therefore La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds are useful candidates to investi-gate the relation between the magnetovolume effect and the IEM transition. In the present study, the magnetovolume effects such as the spontaneous magnetostriction and the pressure effects have been investigated, as well as fundamental characteristics of the IEM transition, for La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds. The obtained results are discussed in terms of the spin fluctuations.

II. EXPERIMENT

Alloying of La(Fe$_x$Si$_{1-x}$)$_{13}$ was carried out by arc melting. To homogenize the specimens, the heat treatment was made in an evacuated vacuumed quartz tube at 1320 K for 7 days. The single phase with a cubic NaZn$_{13}$-type structure was identified by x-ray powder diffraction. Magnetization measurements were made with a superconducting quantum interference device (SQUID) magnetometer. Magnetostriction measurements were carried out by a three terminal capacitance method. Thermal expansion was measured with a differential transformer type dilatometer. Mössbauer effect measurements were made with a constant acceleration-type spectrometer. Pressure dependences of the magnetization and of the Curie temperature were measured by using an extraction-type magnetometer equipped with a Cu-Ti pressure clamp cell.[18]

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of magnetization in 0.3 T for the compounds with $x = 0.84$, 0.86, and 0.88. In the range of low temperatures, the magnetization decreases gradually with increasing temperature. Although only a second-order phase transition at the Curie temperature without any drastic anomaly was reported previously,[19] a discontinuous change takes place at 195 K for $x = 0.88$, indicating a first-order transition. Such a first-order phase transition in the present compounds is limited to the higher Fe concentration region. Indeed, the magnetization gradually decreases
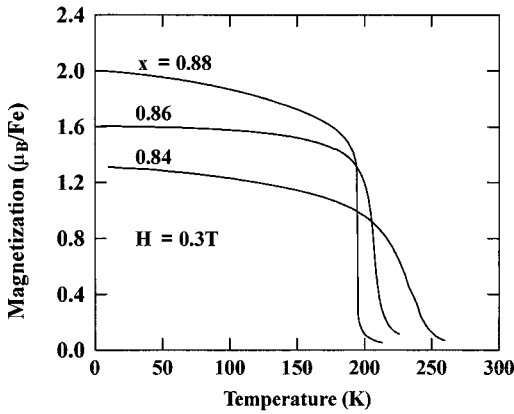
FIG. 1. Temperature dependence of the magnetization for the La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds with $x=0.88$, 0.86, and 0.84.

FIG. 3. Magnetic phase diagram of La(Fe$_x$Si$_{1-x}$)$_{13}$. T_{C2} and T_{C1} denote the Curie temperature of the second-order and the first-order ferromagnetic-paramagnetic transition, respectively. T_0 stands for the critical temperature of metamagnetic transition.

with increasing temperature indicating the second-order phase transition for the compound with $x<0.84$. The Mössbauer spectrum for $x=0.88$ at 193 K shows one sextet component of the magnetic ordered state and a paramagnetic doublet coexists with a ferromagnetic sextet at 195 K in Fig. 2. The sextet component suddenly disappears and only the doublet component is observed at 197 K. Consequently, the transition of the present compound with $x=0.88$ is not from the ferromagnetic to the antiferromagnetic state, which is often observed in some Fe-based compounds,[20,21] but to the paramagnetic state. The coexistence of the ferromagnetic and the paramagnetic states is due to a supercooling phenomenon, being the characteristic feature of the first-order phase transition. Detailed analyses of the Mössbauer spectra will be published elsewhere.

It is considered that the free energy as a function of uniform magnetization M for the present compound with $x=0.88$ has two minima at $M=0$ and $M\neq0$, which respectively correspond to the paramagnetic and the ferromagnetic states. Under these conditions, the free energy structure gives not only the thermal induced first-order phase transition between the ferromagnetic (F) and the paramagnetic (P) states, but also the magnetic-field induced metamagnetic transition from the P states to the F state above the Curie temperature
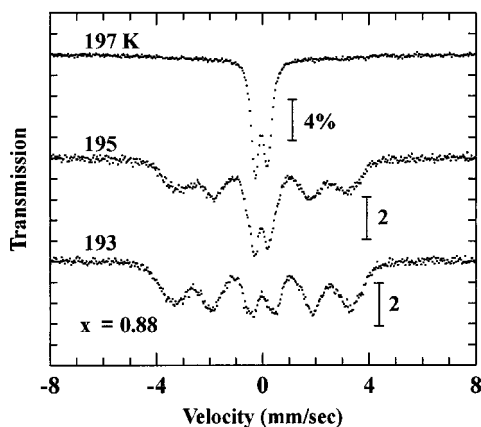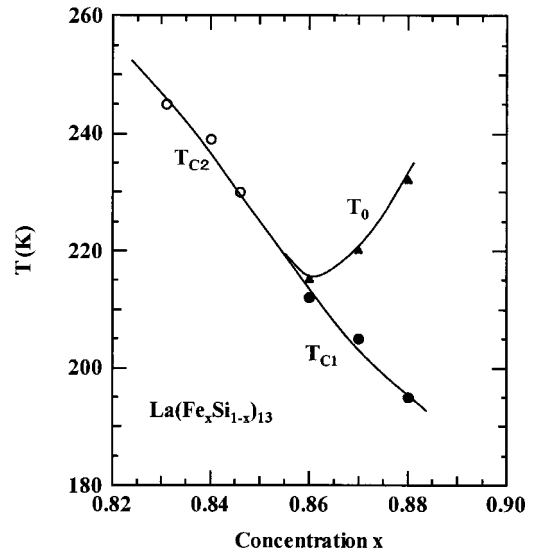
T_{C1} as reported in Ref. 16. The onset of the itinerant-electron metamagnetic transition is conclusive evidence in support of the double minimum structure of free energy. The thermal energy makes the minimum in the ferromagnetic state shallower and the minimum in the paramagnetic state becomes stable above T_{C1}. In other words, the thermal induced first-order phase transition at T_C corresponds to the itinerant-electron metamagnetic transition at the critical magnetic field $B_C=0$. By carrying out the magnetization measurement for the compounds with different concentrations above T_{C1}, the magnetic phase diagram is established as shown in Fig. 3. In $x\leq0.84$, the second-order magnetic phase transition from the ferromagnetic to paramagnetic transition is observed at the Curie temperature T_{C2}. The critical temperature T_0 is conventionally defined as the temperature where hysteresis in the magnetization curves disappears. The Curie temperature T_{C1} decreases, whereas T_0 increases with increasing Fe concentration, indicating that the IEM transition occurs in a wide temperature range. In theoretical calculations for itinerant-electron systems with the negative mode-mode coupling among spin fluctuations,[12,22] the phase boundaries are derived from the critical conditions as a function of the mean square amplitude of spin fluctuations $\xi_p(T)^2$. By assuming a proportional relation between $\xi_p(T)^2$ and temperature T, and neglecting the concentration dependence of the dispersion of spin fluctuations, T_0 decreases with decreasing T_{C1}. It has been reported that the calculated phase diagrams well reproduce the experimental results for the itinerant-electron metamagnetic Co pyrite[8] and Laves phase compounds,[23] though the concentration dependence of T_0 is slightly different between these systems. In contrast to these data, the present T_0 increases with decreasing T_{C1}. These different behaviors may be concerned with the concentration dependence of the damping and dispersion coefficients of spin fluctuations,
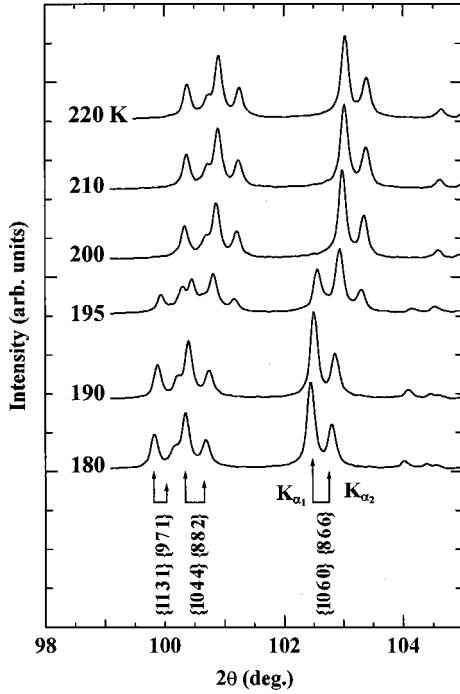

FIG. 2. Mössbauer spectra of the compound with $x=0.88$ recorded at 193, 195, and 197 K.

FIG. 4. X-ray diffraction profiles at various temperature for $x=0.88$. Six sets of planes are indexed by arrows.

FIG. 5. Thermal expansion curves of the compounds with $x=0.84$, 0.86, and 0.88. Solid circles are the data obtained from x-ray diffraction.

which should be measured by microscopic dynamical experiments such as neutron scattering and NMR.

The IEM transition is often followed by significant magnetovolume effects due to an abrupt change in the local magnetic moment.[24,25] Figure 4 shows x-ray diffraction profiles for $x=0.88$ measured in the temperature range crossing the Curie temperature 195 K. No difference between the diffraction patterns of the profiles at 180 and 200 K is confirmed for six sets of planes indexed in Fig. 4, although a significant shift of the peak positions is observed. Therefore the onset of the ferromagnetic ordering has no influence on the symmetry of the atomic lattice, but results in a large volume change. In more detail, the volume change occurs discontinuously, that is, a large volume phase coexists with a small volume phase as seen from the profiles at 170–190 K. The discontinuous change of the volume and the coexistence of the large and small volume phases are attributed to the first-order transition between the F and the P phases and the supercooling effect around the transition temperature, in accord with the Mössbauer spectra shown in Fig. 2. In other words, the onset of the magnetic moment at the transition temperature brings about a significant volume expansion, being about 1.2% in the temperature range of 170–250 K or $0.7\,T_{C1}\sim1.1\,T_{C1}$.

The double minimum structure of free energy $E(T,M)$ is phenomenologically described by the Ginzburg-Landau-type expansion in terms of the series of the magnetization as follows:[9,12]

$$E(T,M)=F_2(T)M(T)^2+F_4(T)M(T)^4+F_6(T)M(T)^6 \quad (1)$$

with $F_2(0)>0$, $F_4(0)<0$, and $F_6(0)>0$. The negative F_4 gives the negative mode-mode coupling among spin fluctua-
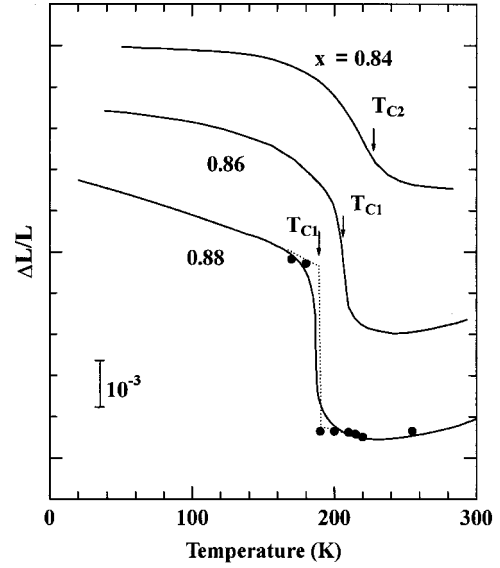
tions and has important influences not only on the IEM transition but also on the magnetovolume effects characterized by a significant spontaneous volume magnetostriction.[13,14] For example, the first principles calculation predicts a double minimum structure of free energy as a function of magnetization and volume for Fe_3Pt ordered and disordered fcc alloys, and the magnetovolume effects in Fe_3Pt is discussed in terms of the energy barrier between these local minima.[14] It should be emphasized that the theoretical calculation by a fixed spin moment method gives the first-order F-P transition in Fe_3Pt ordered alloy,[14] though a martensitic transformation prevents from observing such a magnetic phase transition. On the other hand, the present compounds yield the first-order magnetic phase transition without any change in the crystal structure. Therefore the magnetovolume effects in the ferromagnetic state below T_{C1} are of interest in connection with the relation between the negative mode-mode coupling among spin fluctuations.

Shown in Fig. 5 are thermal expansion curves for the compounds with $x=0.84$, 0.86, and 0.88. The obtained results are similar to those reported previously.[26,27] In connection with the change in the feature of the thermomagnetization curves in Fig. 1, the volume change around T_{C1} becomes continuous with decreasing x. The volume decreases from low temperatures up to the Curie temperature in these three specimens, indicating the existence of the spontaneous volume magnetostriction in the F state. Furthermore, the magnitude of the negative thermal expansion coefficient seems to become smaller with decreasing x. The change of the magnitude of the thermal expansion coefficient corresponds to the temperature dependence of the spontaneous volume magnetostriction ω_s, which is generally expressed as follows:[13,14]

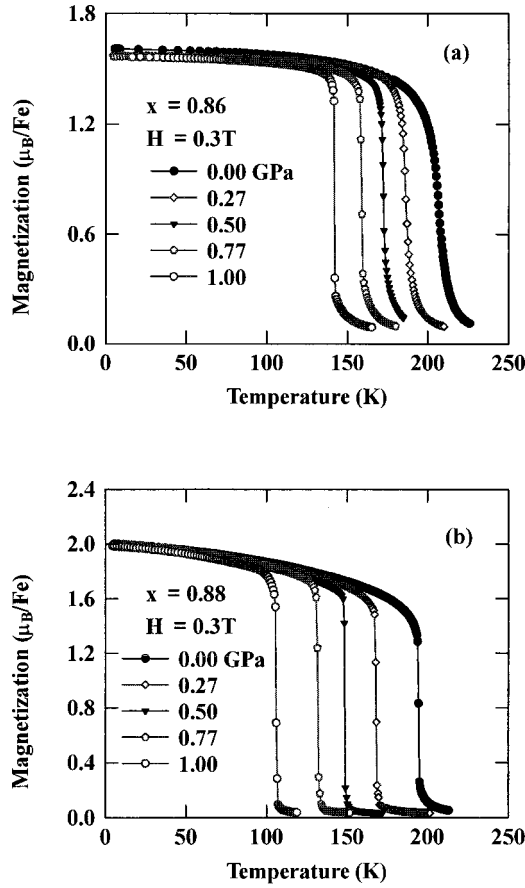$$\omega_s(T)=\kappa C\{M(T)^2+\xi_p(T)^2\}, \quad (2)$$

FIG. 6. Temperature dependence of the magnetization measured in applied hydrostatic pressures for (a) $x = 0.86$ and (b) 0.88.

where κ, C, and ξ_p are the compressibility, the magnetovolume coupling constant, and the amplitude of local thermal spin fluctuations, respectively. With increasing temperature, the magnetization $M(T)$ decreases, while thermal spin fluctuations are excited and then $\xi_p(T)^2$ increases. Therefore a smaller magnitude of the thermal expansion coefficient means a smaller temperature dependence of $M(T)$ and/or steep increase of thermal spin fluctuations. Accordingly, the significant spontaneous volume magnetostriction in the F state is attributed to the negative mode-mode coupling among spin fluctuations.

Since a large volume change is followed by the phase transition in the present system, a significant influence of the hydrostatic pressure to the phase transition is expected. Figures 6(a) and (b) show the temperature dependence of magnetization under hydrostatic pressure for $x = 0.88$ and 0.86, respectively. A strong decrease in the Curie temperature T_{C1} is observed with increasing pressure. Especially, the discontinuous change of magnetization for $x = 0.86$ becomes more significant with increasing pressure, indicating the sharper metamagnetic transition.

The pressure P dependence of the magnetization M, and of the Curie temperature T_{C1} is shown in Figs. 7(a) and (b), respectively. Both the magnetization and the Curie temperature exhibit a negative pressure dependence and the pressure coefficient $\partial \ln M / \partial P$ is -0.015 and -0.019 GPa^{-1}, while $\partial \ln T_{C1} / \partial P$ becomes -0.31 and -0.48 GPa^{-1} for $x = 0.86$
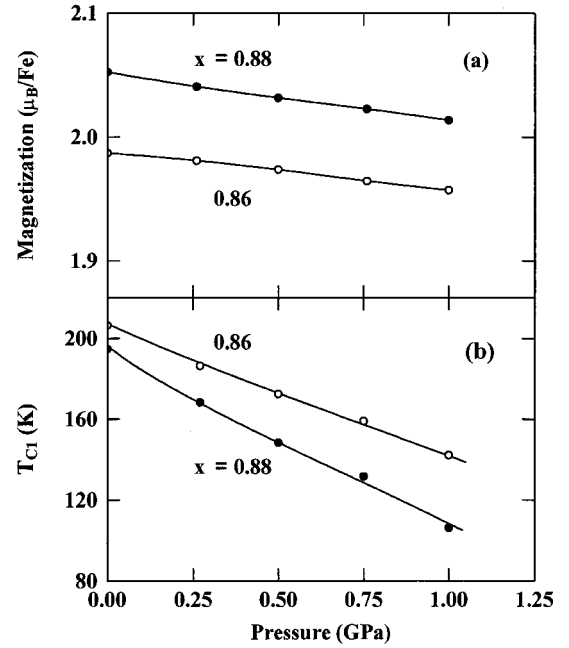

FIG. 7. Pressure dependence of (a) the magnetization and (b) the Curie temperature for $x = 0.86$ and 0.88.

and 0.88, respectively. By neglecting the influence of zero-point spin fluctuations, the pressure dependence of magnetization at low temperatures is mainly due to a change of the width of $3d$ electron band, whereas that of the Curie temperature is connected with the balance between the magnetovolume effect caused by both the pressure and the spin fluctuations.[28] By using the Landau expansion, the critical pressure for the first-order transition from the ferromagnetic to the paramagnetic state is expressed as follows:

$$P_c(T) = P(0) + f_p^a \xi_p(T)^2 + f_p^b \xi_p(T)^4, \qquad (3)$$

where f_p^a and f_p^b are the constants related to magnetovolume coupling constant κC in Eq. (2) and the coefficients $F_2(0)$, $F_4(0)$, and $F_6(0)$ in Eq. (1). The temperature dependence of $\xi_p(T)^2$ is given by

$$\xi_p(T)^2 = \frac{\gamma}{D} \frac{(k_B T)^2}{6\pi F_2(0)}. \qquad (4)$$

The parameters γ and D are concerned with the damping and the dispersion coefficients of spectrum of spin fluctuations.[12] The critical pressure at the constant temperature in Eq. (3) gives the critical temperature at the constant pressure. As shown by the solid lines in Fig. 7(b), the present data are well reproduced by Eq. (3). It should be noted that the critical pressure P_c in Eq. (3) is not a function of M but only $\xi_p(T)^2$. In the itinerant-electron system, it is well known that the curve of the free energy $E(M,T)$ itself is changed by spin fluctuations. The hydrostatic pressure enhances the thermal change in the curve of $E(M,T)$ due to spin fluctuations, and hence a local minimum in the ferromagnetic state steeply becomes shallow, resulting in the lower first-order T_{C1}. Consequently, the influence of pressure on the Curie temperature

is larger than that on M. Strong volume dependence of the Curie temperature T_{C1} is also observed in La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_y$ hydrogenated compounds. In these compounds, the volume expansion due to the hydrogen absorption results in a significant increase in the Curie temperature with respect to the hydrogen concentration y. These results are also interpreted by strong magnetovolume effect of the present compounds.[29,30]

The Landau expansion gives the following another important relation between the Curie temperature T_{C1} and the discontinuous change of magnetization at T_{C1}, $\Delta M(T_{C1})$,[12,31]

$$\Delta M(T_{C1})^2 = \frac{3}{4} \frac{\left| F_4(0) + \frac{14}{3} F_6(0) \xi_p(T_{C1})^2 \right|}{F_6(0)}. \quad (5)$$

Figure 8 shows the relation between $\Delta M(T_{C1})^2$ and T_{C1}^2 for $x=0.86$ and 0.88. In both the compounds, the linear relation between $\Delta M(T_{C1})^2$ and T_{C1}^2 is confirmed. Consequently, these results mean that the pressure effect on T_{C1} is well explained by the Landau expansion. Validity of Eq. (5) strongly implies that the pressure effect on T_{C1} is dominated by spin fluctuations.

In conclusion, a first-order phase transition between the ferromagnetic and the paramagnetic state was observed in La(Fe$_x$Si$_{1-x}$)$_{13}$ compound. The itinerant metamagnetic transition is induced by external magnetic field, above the Curie temperature. A large volume change was observed in both the first-order transition at the Curie temperature and the IEM transition. These results are explained in terms of the double minimum structure in the free energy as a function of magnetic moment (M) and volume (V), that is, these phase transitions are caused by the difference in the energy gain against temperature or magnetic field for a large V state with
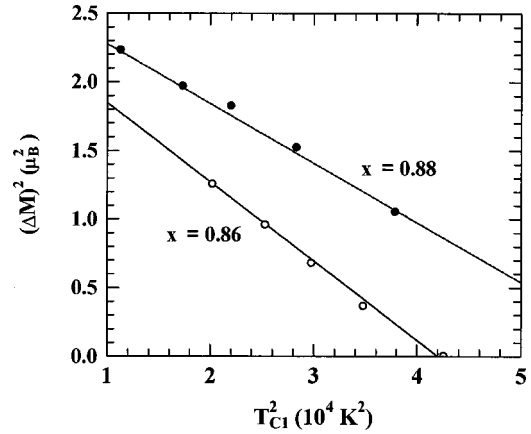

FIG. 8. Square of the discontinuous change of magnetization at the Curie temperature plotted against T_{C1^2} obtained in various hydrostatic pressures for $x=0.86$ and 0.88.

$M\neq0$ and a small V state with $M=0$. At finite temperatures, the IEM transition and the significant magnetovolume effects in the present compounds are influenced by the negative mode-mode coupling among spin fluctuations. The hydrostatic pressure enhances the thermal change in the curve of free energy due to spin fluctuations, and a significant decrease in the Curie temperature is observed by applying hydrostatic pressure.

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