Itinerant-electron metamagnetism and giant magnetocaloric effect

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An isothermal magnetic entropy change in itinerant-electron systems is discussed on the theory of itinerant-electron metamagnetism. The effect of spin fluctuations is taken into account based on the phenomenological Ginzburg-Landau theory. By the Clausius-Clapeyron relation, the magnetic entropy change depends not only on the magnetization jump at the Curie temperature T_C, but also on the temperature dependence of the critical field of the metamagnetic transition. It is shown that the magnetic entropy change at low fields becomes maximum when T_C is about half of the temperature T_{max} where the susceptibility reaches a maximum. The isothermal magnetic entropy changes for $3d$ compounds $Co(S,Se)_2$, $Lu(Co,Al)_2$, and $Lu(Co,Ga)_2$ and also for itinerant $5f$ compound U(Co,Fe)Al are estimated and compared with those observed for MnFe(P,As) and $La(Fe,Si)_{13}$. It has been found generally that the giant magnetocaloric effect in itinerant-electron metamagnets is expected when the coefficient b_0 of M^4 in the Landau energy expansion with respect to the magnetization M is negative and large.

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I. INTRODUCTION

Some intermetallic compounds, which exhibit either temperature- or field-induced first-order magnetic phase transitions, have recently attracted much attention not only for the fundamental magnetism but also for the application to materials science. This is because they are promising materials for magnetic refrigeration.[1,2] For the rare-earth compounds RCo_2, where $R=$ Dy, Ho, and Er, a first-order transition takes place at the Curie temperature T_C. Above T_C, a field-induced metamagnetic transition occurs. A giant magnetocaloric effect is found, which is associated with these first-order transitions of the ferromagnetic moment in RCo_2.[3,4] Such first-order phase transitions are observed even in $3d$ transition-metal compounds without rare-earth elements. The field-induced transition is so-called *itinerant-electron metamagnetism* (IEM).[5,6]

For itinerant-electron metamagnets, the first-order transition of magnetization may take place at T_C. Above T_C, the metamagnetic transition (MT) occurs from the paramagnetic state to the ferromagnetic one under magnetic fields.[6,7] These characteristic magnetic properties are actually observed in $Co(S,Se)_2$, $Lu(Co,Al)_2$, $Lu(Co,Ga)_2$, and others, which are well explained by the theory of IEM.[8,9] In the theory, the effect of spin fluctuations is taken into account based on the phenomenological Ginzburg-Landau theory. The magnetic behavior of these itinerant-electron metamagnets is similar to those of MnFe(P,As) (Ref. 10) and $La(Fe,Si)_{13}$ (Ref. 11), which are promising materials for a magnetic refrigerator.

In this paper, the isothermal magnetic entropy change for these compounds is discussed, based on the theory of IEM. In Sec. II, the magnetic equation of state is given, by taking into account the effect of spin fluctuations. In Sec. III, temperature and magnetic field dependences of magnetization are calculated numerically. The isothermal magnetic entropy change is obtained in Sec. IV. In Sec. V, estimations of the entropy change for $Co(S,Se)_2$, $Lu(Co,Al)_2$, and $Lu(Co,Ga)_2$ are performed and the possibilities of the material of a magnetic refrigerator are discussed. In Sec. VI, the present theory is extended to the case of uniaxial itinerant-electron metamagnets and the entropy change of U(Co,Fe)Al is estimated. A conclusion and discussion are given in Sec. VII.

II. EQUATION OF STATE

In the Landau theory, expanded up to the M^6 term, the equation of state for the magnetic moment M and magnetic field B is given by

$$B=a(T)M+b(T)M^3+c(T)M^5. \tag{1}$$

By the spin fluctuation theory based on the Ginzburg-Landau theory,[8,9] the Landau coefficients $a(T)$, $b(T)$, and $c(T)$ in Eq. (1) are found to be renormalized by spin fluctuations as

$$a(T)=a_0+\frac{5}{3}b_0\xi_T(T)^2+\frac{35}{9}c_0\xi_T(T)^4,$$

$$b(T)=b_0+\frac{14}{3}c_0\xi_T(T)^2,$$

$$c(T)=c_0, \tag{2}$$

where $\xi_T(T)^2$ is the mean-square amplitude of *thermal* spin fluctuations, which is known to increase with increasing T as T^2 at low T. This is derived by the fluctuation-dissipation theorem with dynamical spin susceptibility.[12,13] The coefficients a_0, b_0, and c_0 in Eq. (2) are those renormalized by the *zero-point* spin fluctuations,[14] where the magnetic field dependences of spin fluctuations are neglected.

The MT takes place when the following conditions are satisfied:[15]

$$a(T)>0, \quad b(T)<0, \quad c(T)>0,$$

$$3/16<a(T)c(T)/b(T)^2<9/20. \tag{3}$$

The critical value for the vanishing of the MT is given by $a_0c_0/b_0^2=9/20$, where the critical field B_0 is given by

$$B_0=\frac{4}{5}|b_0|M_0^3. \tag{4}$$

Here, M_0 in Eq. (4) is the magnetic moment at B_0, given by

$$M_0=\sqrt{3|b_0|/10c_0}. \tag{5}$$

Equations (4) and (5) are those at the quantum-critical end point of the MT given in Ref. 16.

On the other hand, the susceptibility maximum is given by $\partial a(T)/\partial \xi(T)^2=0$, because $a(T)$ in Eq. (2) is the inverse of susceptibility and $\xi_T(T)^2$ is a monotonically increasing function of T. One gets[9]

$$\xi_T(T_{max})^2=\frac{3}{14}\frac{|b_0|}{c_0}. \tag{6}$$

Dividing B and M in Eq. (1) by B_0 and M_0 and $\xi_T(T)^2$ in Eq. (2) by $\xi_T(T_{max})^2$, respectively, we get

$$\tilde{B}=\frac{25}{6}\tilde{a}(T)\tilde{M}-\frac{5}{4}\tilde{b}(T)\tilde{M}^3+\frac{3}{8}\tilde{c}(T)\tilde{M}^5, \tag{7}$$

where

$$\tilde{B}=B/B_0, \quad \tilde{M}=M/M_0,$$

$$\tilde{T}^2=\xi_T(T)^2/\xi_T(T_{max})^2=(T/T_{max})^2 \tag{8}$$

and

$$\tilde{a}(T)=a_0c_0/b_0^2-\frac{5}{14}\tilde{T}^2+\frac{5}{28}\tilde{T}^4,$$

$$\tilde{b}(T)=1-\tilde{T}^2, \quad \tilde{c}(T)=1. \tag{9}$$

Here, we make use of the fact that $\xi_T(T)^2$ is proportional to T^2. It should be noted here that the scaled Landau coefficients $\tilde{a}(T)$, $\tilde{b}(T)$, and $\tilde{c}(T)$ are given by a_0c_0/b_0^2 and T/T_{max} only.

III. TEMPERATURE AND FIELD DEPENDENCES OF MAGNETIZATION

Figure 1 denotes the magnetic phase diagram calculated by Eq. (7) for $a_0>0$, $b_0<0$, and $c_0>0$.[6] For $a_0c_0/b_0^2<5/28$, the second-order transition takes place at $\tilde{T}_C$ $(=T_C/T_{max})$ given by

$$\tilde{T}_C^2=1+2\sqrt{7/5}\sqrt{5/28-a_0c_0/b_0^2}. \tag{10}$$

For $5/28<a_0c_0/b_0^2<3/16$, on the other hand, the first-order transition takes place at $\tilde{T}_1$ $(=T_1/T_{max})$ given by

$$\tilde{T}_1^2=1-4\sqrt{7}\sqrt{a_0c_0/b_0^2-5/28}. \tag{11}$$

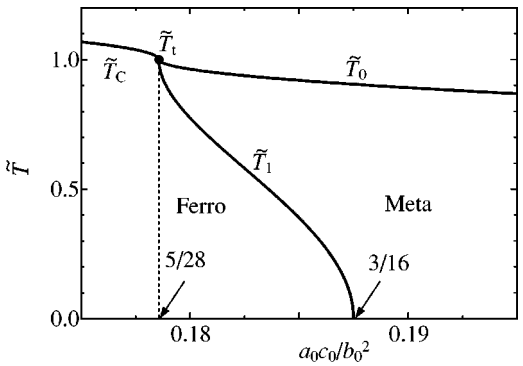

FIG. 1. Calculated magnetic phase diagram. In the range of $a_0c_0/b_0^2<5/28$, the second-order transition takes place at $\tilde{T}_C$. At $5/28<a_0c_0/b_0^2<3/16$, the first-order transition occurs at $\tilde{T}_1$. The MT disappears at $\tilde{T}_0$.

The MT disappears at $\tilde{T}_0$ $(=T_0/T_{max})$ given by

$$\tilde{T}_0^2=1-\sqrt{70/19}\sqrt{a_0c_0/b_0^2-5/28}. \tag{12}$$

$\tilde{T}_t$ in Fig. 1 denotes the triple point where $\tilde{T}_C=\tilde{T}_1=\tilde{T}_0$.

Figure 2 denotes the calculated $\tilde{M}(T,B)$ for $a_0c_0/b_0^2=0.185$, where the first-order transition takes place at $\tilde{T}_1$. The field-induced MT is seen at the temperature between $\tilde{T}_1$ and $\tilde{T}_0$. The critical field $\tilde{B}_C$ $(=B_C/B_0)$ is estimated numerically by comparing the free energies in the ferromagnetic state and the paramagnetic one. On the other hand, the magnetization at low fields shows a maximum in its T dependence at $\tilde{T}>\tilde{T}_0$. Figure 3 denotes the T dependences of the critical field $\tilde{B}_C$ of the MT and the field $\tilde{B}_{max}$ where the magnetization reaches a maximum for $a_0c_0/b_0^2=0.185$. The solid circle denotes the critical field $\tilde{B}_C(T_0)$ at $T=T_0$, where $\tilde{B}_C$ coincides with $\tilde{B}_{max}$. The value of $\tilde{B}_C$ increases with increasing $\tilde{T}$ at low $\tilde{T}$. However, it reaches a maximum and, then decreases with increasing $\tilde{T}$ up to $\tilde{T}_0$.

In Fig. 4, the T dependences of $\tilde{M}$ for $a_0c_0/b_0^2=0.185$ at $\tilde{B}=0.008$, 0.010, and 0.012 are shown by curves (1), (2), and (3), respectively. Two first-order transitions can be seen in curve (2) at $\tilde{B}=0.010$, which is larger than $\tilde{B}_C(T_0)$ shown in Fig. 3. The transition at the higher temperature denotes reen-

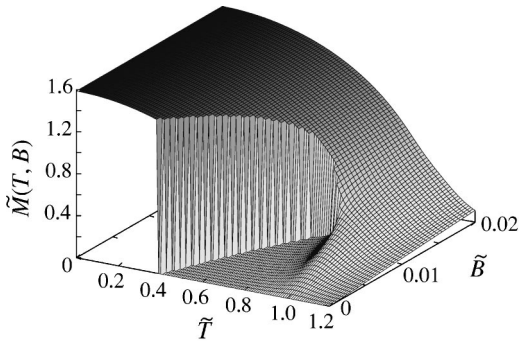

FIG. 2. Calculated result of $\tilde{M}(T,B)$ for $a_0c_0/b_0^2=0.185$.

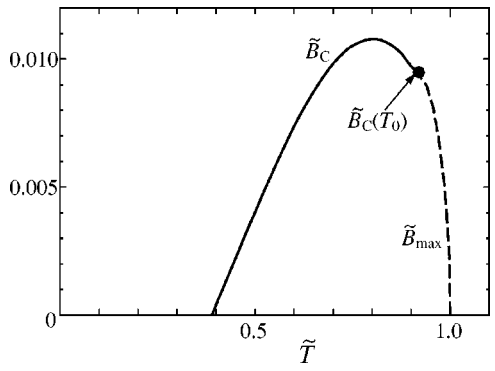

FIG. 3. Calculated results of $\tilde{B}_C$ and $\tilde{B}_{max}$ for $a_0c_0/b_0^2=0.185$.

trant ferromagnetism. This is different from thermal ferromagnetism discussed in Ref. 17, where the ferromagnetic moment appears at finite T without magnetic fields. Moriya[8] pointed out that the negative mode-mode couplings among the spin fluctuations do not lead to such a T-induced ferromagnetism. However, the T-induced ferromagnetism may occur at a certain range of the magnetic field for $5/28 < a_0c_0/b_0^2 < 3/16$. On the other hand, $\tilde{M}$ at $\tilde{B}=0.008$, which is smaller than $\tilde{B}_C(T_0)$ shown in Fig. 3, shows only a maximum above $\tilde{T}_0$, as shown by curve (1) in Fig. 4. The value of $\tilde{M}$ above $\tilde{T}_0$ increases with decreasing $\tilde{T}$ and, then the reentrant ferromagnetic moment appears at $\tilde{T}_0$ suddenly.

IV. MAGNETIC ENTROPY CHANGE

The isothermal magnetic entropy change $\Delta S_m(T,B)$ $[=S_m(T,B)-S_m(T,0)]$ between the magnetic fields B and $B=0$ is given by the following expression associated with the Maxwell relation:

$$\Delta S_m(T,B)=\int_0^B dB'(\partial M/\partial T)_{B'}, \tag{13}$$

which is rewritten in terms of $\tilde{M}$, $\tilde{B}$, and $\tilde{T}$ by

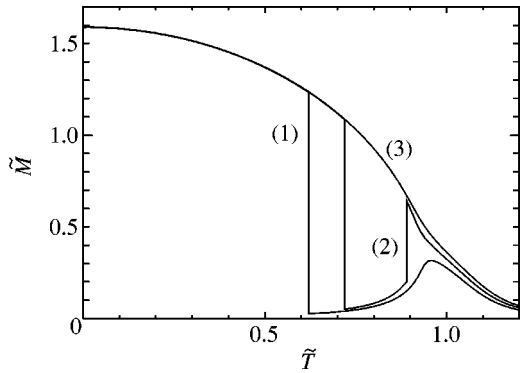

FIG. 4. Calculated results of $\tilde{M}$. Curves (1), (2), and (3) are those calculated at $\tilde{B}=0.008$, 0.010, and 0.012, respectively, for $a_0c_0/b_0^2=0.185$.

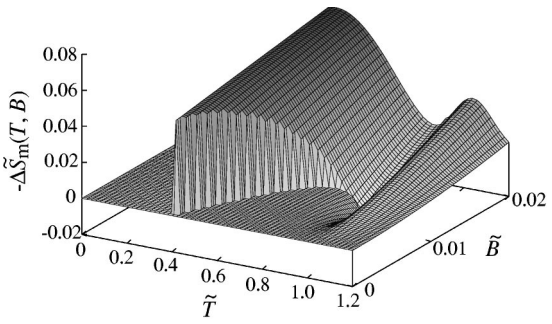

FIG. 5. Magnetic entropy change $-\Delta\tilde{S}_m(T,B)$ calculated from $\tilde{M}(T,B)$ shown in Fig. 2 for $a_0c_0/b_0^2=0.185$.

$$\Delta\tilde{S}_m(T,B)=\int_0^{\tilde{B}} d\tilde{B}'(\partial\tilde{M}/\partial\tilde{T})_{\tilde{B}'}, \tag{14}$$

where

$$\Delta\tilde{S}_m(T,B)=\Delta S_m(B,T)/S_0 \tag{15}$$

and

$$S_0=B_0M_0/T_{max}. \tag{16}$$

Here, B_0, M_0, and T_{max} are given by Eqs. (4), (5), and (6), respectively.

Figure 5 denotes the magnetic entropy change calculated from $\tilde{M}(T,B)$ for $a_0c_0/b_0^2=0.185$ shown in Fig. 2. Negative and large entropy changes are obtained along the critical field $\tilde{B}_C$, while positive and small changes are obtained in a narrow region where $(\partial\tilde{M}/\partial\tilde{T})_{\tilde{B}}$ is positive near $\tilde{T}=1$. In Fig. 6, magnetic entropy changes $-\Delta\tilde{S}_m$ at $\tilde{B}=0.3\times10^{-2}$, 0.6×10^{-3}, 0.9×10^{-3}, and 1.2×10^{-3} are shown by curves (1)–(4), respectively.

In Fig. 7, magnetic entropy changes $-\Delta\tilde{S}_m$ at $\tilde{B}=0.1\times10^{-2}$ for $a_0c_0/b_0^2=0.178$–0.187 are shown by curves (1)–(10), respectively. It is seen that $-\Delta\tilde{S}_m$ becomes maximum around $\tilde{T}=0.5$. This is because the magnetic entropy change depends not only on the magnetization jump at T_C, but also on the T dependence of B_C, associated with the Clausius-Clapeyron relation. At $T=T_1(B)$, one gets

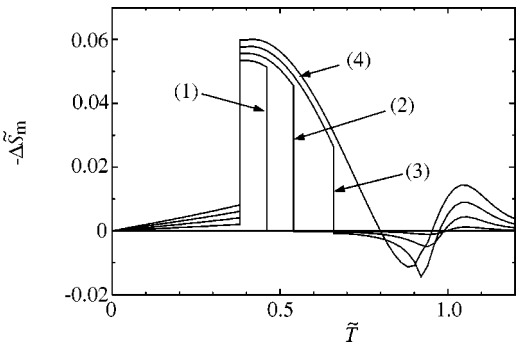

FIG. 6. Magnetic entropy changes $-\Delta\tilde{S}_m$. Curves (1), (2), (3), and (4) are those calculated at $\tilde{B}=0.3\times10^{-2}$, 0.6×10^{-2}, 0.9×10^{-2}, and 1.2×10^{-2}, respectively, for $a_0c_0/b_0^2=0.185$.

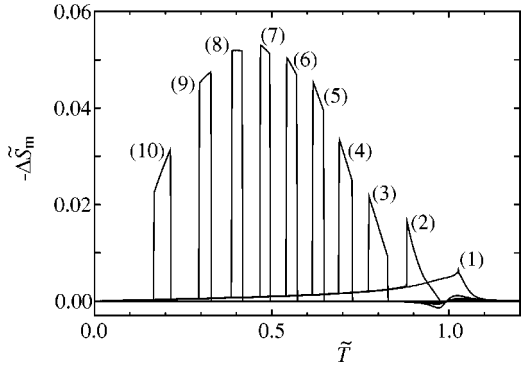

FIG. 7. Magnetic entropy changes $-\Delta\tilde{S}_m$ at low field, $\tilde{B}=0.1\times10^{-2}$. Curves (1)–(10) are those for $a_0c_0/b_0^2=0.178$–0.187 at an interval of 0.01.

$$\left(\frac{\partial M}{\partial T}\right)_B = -|\Delta M|\,\delta(T-T_1(B))$$

$$= -\left(\frac{|\Delta M|}{|\partial T_1/\partial B|}\right)\delta(B-B_C(T)), \qquad (17)$$

where ΔM is the magnetization jump at T_C; then we get

$$\Delta S_m = -|\Delta M|/|\partial T_1/\partial B|. \qquad (18)$$

This is just the Clausius-Clapeyron relation.

Equation (18) is rewritten by

$$\Delta\tilde{S}_m = -\left(\frac{\partial\tilde{B}_C}{\partial\tilde{T}}\right)|\Delta\tilde{M}|, \qquad (19)$$

where $\Delta\tilde{M}=\Delta M/M_0$. Here, $(\partial\tilde{B}_C/\partial\tilde{T})$ is positive when $\tilde{B}_C$ is small. Figure 8 denotes the critical field $\tilde{B}_C$ calculated for $a_0c_0/b_0^2=0.180$–0.189. The value of $\partial\tilde{B}_C/\partial\tilde{T}$ becomes zero at both ends of the Curie temperatures $\tilde{T}_1=0$ $(a_0c_0/b_0^2=3/16)$ and $\tilde{T}_1=1$ $(a_0c_0/b_0^2=5/28)$. In Fig. 9, the calculated results of $\tilde{T}_1$, $|\Delta\tilde{M}|$, $d\tilde{B}_C/d\tilde{T}$, and $-\Delta\tilde{S}_m$ are shown as a function of a_0c_0/b_0^2. As the value of $\tilde{T}_1$ is given as a function of a_0c_0/b_0^2, then, $|\Delta\tilde{M}|$, $d\tilde{B}_c/d\tilde{T}$, and $-\Delta\tilde{S}_m$ are obtained as a function of T_1, which are shown in Fig. 10.

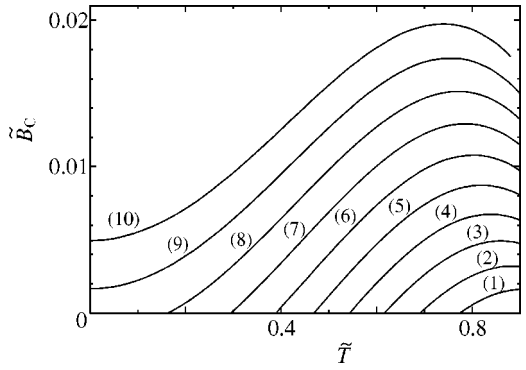

FIG. 8. Critical fields $\tilde{B}_C$ as a function of $\tilde{T}$. Curves (1)–(10) are those for $a_0c_0/b_0^2=0.180$–0.189 at an interval of 0.01.

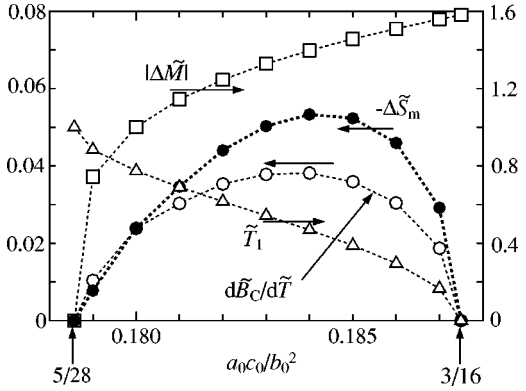

FIG. 9. Calculated values of $\tilde{T}_1$, $|\Delta\tilde{M}|$, $d\tilde{B}_C/d\tilde{T}$, and $-\Delta\tilde{S}_m$ as a function of a_0c_0/b_0^2.

The maximum value of the reduced entropy change $-\Delta\tilde{S}_m$ is estimated to be 0.0533 at $\tilde{T}_1\sim0.5$. The scaling factor S_0 is an important quantity for the estimation of the entropy change.

V. ESTIMATION OF S_0

The pyrite compounds $Co(S_{1-x}Se_x)_2$ $(0<x<0.1)$ show the first-order transition at the Curie temperature T_1. Above T_1 they show the metamagnetic transition.[18] Cubic Laves phase compounds $Lu(Co_{1-x}Al_x)_2$ around $x\sim0.095$ and $Lu(Co_{1-x}Ga_x)_2$ around $x\sim0.1$ also show the first-order transition at T_1.[19,20] For these compounds the Landau coefficients a_0, b_0, and c_0 are estimated from the observed magnetization curves at low temperature. Then, the magnetic moment M_0 and the critical field B_0 at the critical end point of the MT can be obtained by Eqs. (4) and (5). The observed value of T_{max} for $Co(S,Se)_2$ is 80 K, while we have no observed data of T_{max} for $Lu(Co,Al)_2$ and $Lu(Co,Ga)_2$. Then, we take T_{max} for these Lu compounds as the observed values of T_t at the triple point, as $T_{max}=T_t$.

The scaling factors S_0 estimated from Eq. (16) are shown in Table I, together with the values of M_0, B_0, and T_{max}. It is noted that the value of S_0 for $Co(S,Se)_2$ is large and the maximum value of $-\Delta S_m$ becomes 11 J/kg K, which is al-

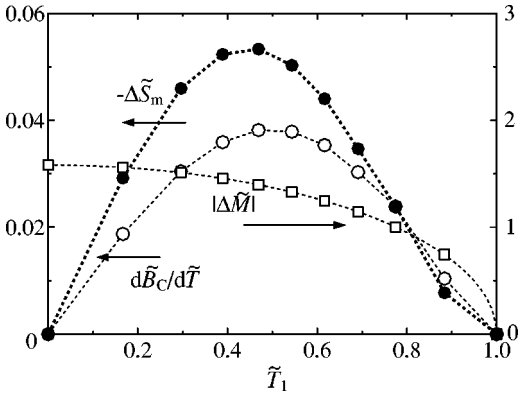

FIG. 10. Calculated values of $|\Delta\tilde{M}|$, $d\tilde{B}_C/d\tilde{T}$, and $-\Delta\tilde{S}_m$ as a function of $\tilde{T}_1$.

TABLE I. Values of S_0, M_0, and B_0 estimated from the observed data for $Co(S,Se)_2$ (Ref. 18), $Lu(Co,Al)_2$ and $Lu(Co,Ga)_2$ (Ref. 19), MnFe(P,As) (Ref. 10), and $La(Fe,Si)_{13}$ (Ref. 11). The values of S_0, M_0, B_0, and T_{max} for $Co(S,Se)_2$ do not depend on the Se concentration.

	S_0 (J/kg K)	M_0 (μ_B/3d atom)	B_0 (T)	T_{max} (K)
$Co(S,Se)_2$	210	0.51	750	80
$Lu(Co_{0.9}Al_{0.1})_2$	50	0.6	95	40
$Lu(Co_{0.9}Ga_{0.1})_2$	45	0.6	88	40
MnFe(P,As)	610	1.7	3700	700
$La(Fe,Si)_{13}$	560	1.1	2600	400

most the same as that of Gd metal.[1] Then, this compound system is found to be one of promising materials for the magnetic refrigeration in the temperature range below T_{max} ($=80$ K). The value of T_{max} does not depend so much on the concentration x of Se in $Co(S_{1-x}Se_x)_2$. Then, from the x dependence of $-\Delta S_m$ and T_1, the curve of $-\Delta S_m$ shown in Fig. 7 is expected for $0 \leqslant x \leqslant 0.1$. On the other hand, the estimated values of S_0 for $Lu(Co,Al)_2$ and $Lu(Co,Ga)_2$ are found to be very small.

Tegus *et al.*[10] have observed a giant magnetocaloric effect for $MnFeP_{1-x}As_x$ ($0.25 \leqslant x \leqslant 0.65$). This compound shows a large magnetization jump at the Curie temperature T_1 of the first-order transition.[21] The field-induced metamagnetic transition is also observed above T_1. It has been found that the observed value $-\Delta S_m$ for $MnFeP_{1-x}As_x$ decreases with increasing x, although the magnetization jump at T_1 increases. This is probably because the temperature dependence of the critical field B_C of the MT becomes small as x increases. The maximum entropy change is observed to be about 33 J/kg K at $\Delta B=5$ T for $MnFeP_{0.65}As_{0.35}$.[10] Comparing the calculated maximum value of $-\Delta \tilde{S}_m$ with this observed one, we get $S_0=620$ J/kg K. From the observed value of dB_C/dT (~ 0.2 T/K) for this compound, we obtain that $M_0=1.7\mu_B$ per $3d$ atom and $B_0=5.3T_{max}$ T. We have no observed data of T_{max} but the maximum of the entropy change is expected at $\tilde{T}_1 \sim 0.5$. The observed value of T_1 for $MnFeP_{0.65}As_{0.35}$ is about 350 K. Then, we obtain $T_{max} \sim 700$ K and $B_0 \sim 3.7\times 10^3$ T.

Recently, Fujita *et al.*[11] have found a strong magnetocaloric effect for $La(Fe_xSi_{1-x})_{13}$ ($0.86 \leqslant x \leqslant 0.90$). This compound system also shows a first-order transition at T_1. Above T_1, the MT takes place under the magnetic field. Then, the concentration dependence of $-\Delta \tilde{S}_m$ shown in Fig. 7 is expected to be observed. Fujita *et al.*[11] have actually observed that the maximum value of $-\Delta S_m$ increases with increasing x at $0.86 \leqslant x \leqslant 0.90$ for $La(Fe_xSi_{1-x})_{13}$. Similar results have also been observed in $La(Fe,Co)_{11.2}Si_{1.8}$ (Ref. 22) and $LaFe_{11.6}Si_{1.4}C_x$ (Ref. 23).

For $La(Fe_xSi_{1-x})_{13}$, the critical concentration between the first-order and second-order transitions at the Curie temperature is about 0.86.[24] Then, their observed results of $-\Delta S_m$ are similar to our calculated one shown in Fig. 7 at $0.5 < T/T_{max} < 1.0$. The maximum entropy change is observed to be about 30 J/kg K at $\Delta B=5$ T for $La(Fe_{0.9}Si_{0.1})_{13}$.[11] Then, we find that $S_0=560$ J/kg K. From the observed value of dB_C/dT (~ 0.25 T/K) for this compound, we obtain that $M_0=1.1$ μ_B/Fe and $B_0=6.6T_{max}$ T. We have no observed data of T_{max}, but the maximum of the entropy change is expected at $T_1/T_{max} \sim 0.5$. The value of T_1 for $La(Fe_{0.9}Si_{0.1})_{13}$ is about 200 K.[24] Then, we obtain $T_{max} \sim 400$ K and $B_0 \sim 2.6\times 10^3$ T. The values of S_0 per $3d$ transition-metal atom for $Co(S,Se)_2$, MnFe(P,As), and $La(Fe,Si)_{13}$ are almost same order of magnitude with each other.

VI. UNIAXIAL ANISOTROPIC SYSTEM

Metamagnetic behavior discussed in the previous sections is observed even in the $5f$ intermetallic compound UCoAl with the hexagonal ZrNiAl-type structure. The ground state of this compound is paramagnetic. The magnetic susceptibility exhibits a broad maximum in its temperature dependence. In a magnetic field of about 0.6 T applied along the c axis, this compound shows the MT to the ferromagnetic state with a U magnetic moment of $0.3\mu_B$.[25]

On the other hand, the ferromagnetic ground state can be achieved in UCoAl by 2% doping of the Co sublattice by Fe. Mushnikov *et al.*[26] have found that the reentrant metamagnetism of the UCoAl type is observed under the pressure above 0.4 GPa. In the narrow pressure range $0.25 \leqslant P \leqslant 0.33$ GPa, the compound shows a first-order transition at the Curie temperature T_1. The magnetic moment in these U compounds shows a very strong uniaxial anisotropy. Then, the theory given in the previous sections for the isotropic system cannot be used. However, this theory has been extended to the case of a uniaxial metamagnetic system in Ref. 27, where only the longitudinal spin fluctuations are taken into account.

In this case, the Landau coefficients $a(T)$, $b(T)$, and $c(T)$ in the equation of state (1) are given by[27]

$$a(T)=a_0+3b_0\xi_z(T)^2+15c_0\xi_z(T)^4,$$

$$b(T)=b_0+10c_0\xi_z(T)^2,$$

$$c(T)=c_0, \tag{20}$$

where $\xi_z(T)^2$ is the mean-square amplitude of longitudinal magnetization density. Scaling M and B by those at the critical end point of the MT given by Eqs. (4) and (5), one gets the same equation of state for $\tilde{B}$ and $\tilde{M}$ as Eq. (7), where

$$\tilde{a}(T)=a_0c_0/b_0^2-\frac{3}{10}\tilde{T}^2+\frac{3}{20}\tilde{T}^4. \tag{21}$$

The expressions of $\tilde{b}(T)$ and $\tilde{c}(T)$ are the same as those in Eq. (9). The susceptibility maximum temperature T_{max} is given by

$$\xi_z(T_{max})^2=\frac{|b_0|}{10c_0}. \tag{22}$$

$\tilde{T}$ in Eq. (21) is the scaled temperature by T_{max}.

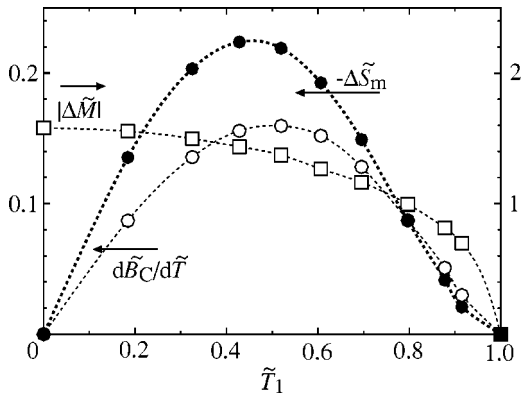

FIG. 11. Calculated values of $|\Delta\tilde{M}|$, $d\tilde{B}_C/d\tilde{T}$, and $-\Delta\tilde{S}_m$ for U(Co,Fe)Al, as a function of $\tilde{T}_1$.

The second-order transition takes place at $\tilde{T}_C$ given by

$$\tilde{T}_C^2 = 1 + \sqrt{20/3}\sqrt{3/20 - a_0c_0/b_0^2}. \tag{23}$$

On the other hand, the first-order transition takes place at the Curie temperature $\tilde{T}_1$ given by

$$\tilde{T}_1^2 = 1 - \sqrt{80/3}\sqrt{a_0c_0/b_0^2 - 3/20}. \tag{24}$$

The MT disappears at $\tilde{T}_0$ given by

$$\tilde{T}_0^2 = 1 - \sqrt{10/3}\sqrt{a_0c_0/b_0^2 - 3/20}. \tag{25}$$

The expressions of $\tilde{T}_C$, $\tilde{T}_1$, and $\tilde{T}_0$ are different from those Eqs. (10)–(12) for the isotropic case. However, the magnetic phase diagrams for anisotropic and isotropic cases are similar to each other.[26]

In Fig. 11 the calculated results for $-\Delta\tilde{S}_m$, $|\Delta\tilde{M}|$, and $d\tilde{B}_C/d\tilde{T}$ are shown as a function of $\tilde{T}_1$. Comparing with Fig. 10, $-\Delta\tilde{S}_m$ for the uniaxial anisotropic case is about 5 times as large as that for the isotropic case. This comes from the strong $\tilde{T}$ dependence of $\tilde{B}_C$, as shown in Fig. 11. However, it does not mean that B_C itself depends strongly on T. As seen in Eqs. (6) and (22), the scaling factor T_{max} in $\tilde{T}$ for the anisotropic case is much lower than that for the isotropic case with the same value of a_0c_0/b_0^2. In fact, the observed value of dB_C/dT for $UCo_{0.98}Fe_{0.02}Al$ is 0.035 T/K under a pressure 0.3 GPa,[26] which is one order of magnitude smaller than that for $Co(S,Se)_2$, $La(Fe,Si)_{13}$, and MnFe(P,As).

The values of B_0 and M_0 in Eqs. (4) and (5) for $UCo_{0.98}Fe_{0.02}Al$ under 0.3 GPa, where the first-order transition at T_1 takes place, are obtained from the estimated values of b_0 and c_0 in Ref. 26 as $0.2\mu_B$ per U atom and 1.3 T, respectively. The observed value of T_{max} is 13 K. From these values, we get $S_0 = 0.3$ J/kg K. The maximum value of $-\Delta S_m$ $(= -\Delta\tilde{S}_m S_0)$ is then found to be very small, 0.07 J/kg K.

VII. CONCLUSION AND DISCUSSION

In this paper, the isothermal entropy change has been discussed, based on the theory of itinerant-electron metamagnetism. The effect of spin fluctuations was taken into account on the phenomenological Ginzburg-Landau theory. The magnetic equation of state for the magnetic field and magnetization can be scaled by these critical values at the end point of the MT and the temperature T_{max}. The scaled equation includes only one parameter a_0c_0/b_0^2.

It has been shown by numerical calculations that temperature-induced ferromagnetism may appear under a finite magnetic field, after the first-order ferromagnetic transition of the magnetization takes place at T_1. This is just reentrant ferromagnetism, which is expected for itinerant-electron metamagnets under strong magnetic fields.

It has been also shown that the isothermal magnetic entropy change depends not only on the magnetization jump at T_1, but also on the temperature derivative of B_C of the MT. The magnetic entropy change $-\Delta\tilde{S}_m$ at low fields has been found to become maximum when the Curie temperature T_1 of the first-order transition is about half of the temperature T_{max}. It should be noted here that both of the scaled entropy change $-\Delta\tilde{S}_m$ and the scaled Curie temperature $\tilde{T}_1$ of the first-order transition are given only by a characteristic quantity a_0c_0/b_0^2. Therefore, $-\Delta\tilde{S}_m$ is given as a function of $\tilde{T}_1$, which makes it possible to compare our calculated results with the observed concentration dependence of $-\Delta S_m$. Our result of $-\Delta\tilde{S}_m$ as a function of $\tilde{T}_1$ is a universal one, being independent of materials for itinerant-electron metamagnets.

The maximum of the isothermal magnetic entropy changes in $Co(S_{1-x}Se_x)_2$ $(0 \leqslant x \leqslant 0.1)$ is rather smaller than that in $MnFeP_{1-x}As_x$ $(0.25 \leqslant x \leqslant 0.65)$ (Ref. 10) and $La(Fe_xSi_{1-x})_{13}$ $(0.88 \leqslant x \leqslant 0.90)$ (Ref. 11) but almost the same as that for Gd metal,[1] even though the Curie temperature is very low. Therefore, the pyrite compound $Co(S,Se)_2$ is considered to be a promising material for the magnetic refrigeration in the temperature range below 80 K.

We have also estimated the entropy change of a uniaxial anisotropic system of U(Co,Fe)Al in Sec. VI. However, the entropy change of this compound has been found to be very small, as well as other itinerant-electron metamagnets $Lu(Co,Al)_2$ and $Lu(Co,Ga)_2$. In this way, some itinerant-electron metamagnets were found to show no giant magnetocaloric effect, although the first-order transition is observed at T_1.

The temperature dependence of B_C of the MT plays an important role in the isothermal magnetic entropy change for itinerant-electron metamagnets. This is also derived from the following consideration. In the limiting case of $a_0c_0/b_0^2 = 3/16$ (i.e., $T_1 = 0$), the critical field B_C of the MT is for the isotropic case is given by[6]

$$B_C = \frac{1}{18}c_0M_1^3\{\xi_T(T)^2 - \xi_T(T_1)^2\}, \tag{26}$$

where M_1 $(= \sqrt{3|b_0|/4c_0})$ is the magnetization jump at T_1. That is, B_C is proportional to $T - T_1$ just above T_1, as $\xi(T)^2$ is to T^2. Equation (26) is rewritten in terms of B_0, M_0, and T_{max} given in Eqs. (4)–(6) as

$$B_C = \frac{5}{84}\sqrt{5/2}\tilde{T}_1(\tilde{T}-\tilde{T}_1)|b_0|M_0^3, \quad (27)$$

at low T_1. The values of M_0 for Co compounds $Co(S,Se)_2$, $Lu(Co,Al)_2$, and $Lu(Co,Ga)_2$ have the same order of magnitude with each other, as shown in Table I. On the other hand, the value of $|b_0|$ estimated from the observed magnetization curve for $Co(S,Se)_2$ at low temperature[18] is very large, 7.1×10^3 $[T/(\mu_B/\text{f.u.})^3]$, comparing with the estimated values of $|b_0|$, 65 and 69 $[T/(\mu_B/\text{f.u.})^3]$, for $Lu(Co,Al)_2$ and $Lu(Co,Ga)_2$.[19,20] In fact, the observed value of dB_C/dT for $Co(S_{0.9}Se_{0.1})_2$ is 0.15 T/K,[18] which is almost the same as the observed value 0.2 T/K for $MnFeP_{0.65}As_{0.35}$ (Ref. 10) and 0.25 T/K for $La(Fe_{0.9}Si_{0.1})_{13}$ (Ref. 11).

It has been also shown in Sec. IV that the magnetic entropy change $-\Delta S_m$ becomes large when S_0 is large. The value of S_0 is proportional to B_0 and then to $|b_0|$ as given by Eq. (4). In this way, b_0 is found to be very important quantity to design giant magnetocaloric materials. It is concluded that the itinerant-electron metamagnets show a giant magnetocaloric effect when the value of b_0 is negative and large. This quantity b_0 can be estimated from *ab initio* calculations of band structure. It should be noted here that a large and negative value of b_0 is obtained when the Fermi level lies near a minimum of density of states with closely neighboring sharp peaks.

Recent renormalization group theories[16,28] show that some corrections to the elementary treatments on the Ginzburg-Landau theory are sometimes significant. For instance, an unexpected temperature variation of the resistivity is obtained on the border of different sort of first-order transitions.[29,30] Moreover, large-amplitude spin fluctuations on the border of the first-order transition may radically change the results for some properties. Nevertheless, the progress of the study in magnetic refrigeration could be accelerated with the help of practical theoretical guidelines given in this paper.

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