Alloying and pressure-induced transitions between 5*f*-band metamagnetism and ferromagnetism

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Effects of external hydrostatic pressure up to 1.2 GPa and the Al-Ga alloying on the magnetism in $UCoAl_{1-x}Ga_x$ compounds have been studied. Ga substitutions for Al in UCoAl lead to gradual transformation of a 5*f*-band metamagnetism towards ferromagnetism (for $x \geq 0.2$). The application of pressure yields reverse effects clearly seen in compounds with $x \leq 0.4$. The spontaneous magnetization μ_s and the Curie temperature T_C of ferromagnetic compounds are gradually suppressed with increasing pressure. The values of $d \ln T_C/dp$ and $d \ln \mu_s/dp$ slowly increase with x decreasing down to 0.4, whereas for $x < 0.4$ an abrupt growth of pressure parameters is observed with further lowering Ga content. This is a fingerprint of a pressure-induced collapse of ferromagnetism and a simultaneous reentrance of the ''UCoAl-type'' metamagnetism in compounds with lower Ga content ($x \leq 0.3$). The observed evolution of magnetism is discussed in terms of pressure and alloying-induced variation of the 5*f*-ligand hybridization that determines both the stability of the U magnetic moment and the strength of U-U exchange interactions. [S0163-1829(99)01826-3]

I. INTRODUCTION

The itinerant electron metamagnetism, first predicted by Wohlfarth and Rhodes[1] for YCo_2, is one of the phenomena manifesting the intimate relationship between electronic structure and magnetism in metals. It is observed in nearly magnetic materials with *d*- or *f*-electron states forming a sufficiently narrow band at E_F and in which spin-fluctuation effects cause a maximum in the temperature dependence of susceptibility around $T_{\max}$. When applying a sufficiently strong magnetic field on such a material at temperatures well below the susceptibility maximum, a first-order transition to the high-magnetization state can be observed. YCo_2 is a prominent example of an itinerant 3*d*-electron metamagnet in which a metamagnetic transition at 4.2 K has been found experimentally in magnetic fields around $B_c = 69$ T.[2] The necessary conditions for the appearance of metamagnetism have been theoretically studied by Yamada.[3]

UCoAl is apparently an itinerant 5*f*-electron metamagnet, which, besides numerous analogies to YCo_2, exhibits also some strikingly different features.[4,5] First, the very low critical field for metamagnetism in UCoAl ($B_c \cong 0.7$ T) is two orders of magnitude lower than in YCo_2. Another fundamental difference consists in the strong uniaxial anisotropy of the metamagnetism in UCoAl, which is not at all observed in fields applied perpendicular to the *c* axis of its hexagonal structure, whereas the 3*d*-electron metamagnetism in YCo_2 and related compounds is isotropic. The latter feature of UCoAl is a consequence of a strong spin-orbit interaction of 5*f* states and the anisotropic two-ion-exchange interaction mediated by the 5*f*-ligand hybridization in U compounds.[6]

The metamagnetism in both the 3*d* systems of the YCo_2 type and the 5*f*-electron representative UCoAl is sensitive to external pressure and to alloying. In both types the external pressure leads to an increase of B_c and $T_{\max}$ (Refs. 2, 4, and 5) driving the system towards Pauli paramagnetism. On the other hand, doping by suitable elements may lead to a decrease of B_c and $T_{\max}$ and finally to a ferromagnetic instability both in the YCo_2-type materials[2] and UCoAl.[4]

An interesting example of a continuous transformation of a metamagnet towards a ferromagnet is represented by substitutions of Ga for Al atoms in UCoAl. All the $UCoAl_{1-x}Ga_x$ compounds possess the hexagonal ZrNiAl-type crystal structure and the lattice parameters are only weakly dependent on the Ga content.[7,8] The other terminal compound of the $UCoAl_{1-x}Ga_x$ system, UCoGa below $T_C = 47$ K is a simple ferromagnet with a U moment $\mu_s = 0.63\,\mu_B$/f.u. (Refs. 9 and 10). Owing to a strong uniaxial anisotropy, the U magnetic moments in both terminal compounds (in ordered state) and presumably also in their solid solutions are aligned along the *c* axis. Besides these considerable U moments, an order of magnitude smaller moments detected on Co atoms[11] can be attributed to polarization of the 3*d* states due to the 5*f*-3*d* hybridization.

When Ga atoms are substituted on Al sites in UCoAl, a spontaneous magnetization connected with the onset of ferromagnetism is indicated already for low values of x in the $UCoAl_{1-x}Ga_x$ system.[7] In this initial regime of doping, however, the spontaneous moment is very small and an additional moment is induced through the metamagnetic transition in low fields yielding above the transition a total value of $\approx 0.3\ \mu_B$/f.u. The gradual stabilization of ferromagnetism up to a stage without any additional metamagnetic transition, which occurs at $x = 0.20$, is accompanied by reduction of the electronic specific-heat coefficient γ by approximately 20%.[8] A comparable reduction of γ is accompanying the metamag-

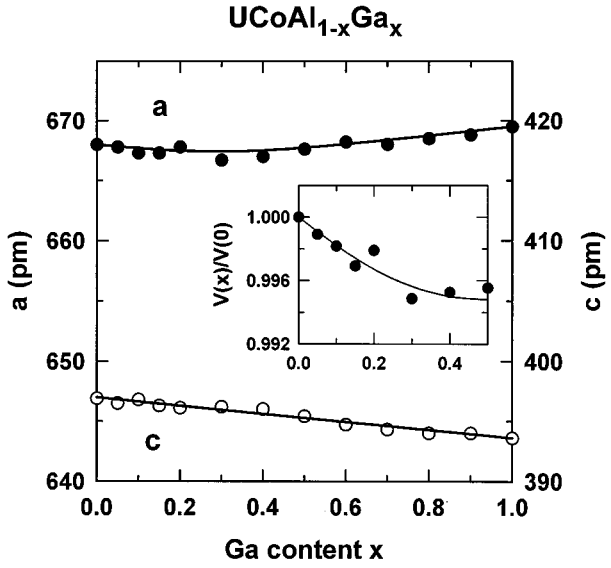

FIG. 1. Concentration dependencies of lattice parameters a and c of the $UCoAl_{1-x}Ga_x$ compounds. The inset shows related change of the unit-cell volume at low-Ga content where we observe the onset of ferromagnetism.

netic transition in UCoAl.[12] In both cases this effect can be attributed to the suppression of $5f$-moment fluctuations. The second drop of the γ value, which takes place between compounds with $x=0.6$ and 0.7, is not reflected in the concentration development of magnetic parameters that is smooth inbetween the two compositions.[8]

In the present paper, we report on the study of pressure influence on magnetic parameters of the $UCoAl_{1-x}Ga_x$ solid solutions within the concentration range where they exhibit stable ferromagnetism in ambient pressure ($0.2 \leqslant x \leqslant 1.0$).

II. EXPERIMENTAL DETAILS

The $UCoAl_{1-x}Ga_x$ alloys have been obtained by melting the corresponding amounts of the elementary metals (purity of U 99.9% and better for other metals) in an arc furnace with protective Ar atmosphere. The ingots (of ~2 g mass) were turned several times and remelted to assure good homogeneity. Then they were wrapped into a Ta foil and annealed at 700 °C for 1 week. The phase composition of the alloys and their lattice parameters were determined by a standard x-ray diffraction. The concentration dependence of lattice parameters is shown in Fig. 1.

The magnetization as a function of magnetic field (up to 9 T) and temperature (in the 4.2–60 K interval) was measured with an extraction-type magnetometer with a superconducting magnet. For the pressure study, samples of approximately 50 mg consisting of small (typical linear dimensions of 0.2–0.5 mm) randomly oriented pieces were compressed in Teflon capsules filled with a liquid-pressure-transmitting medium, a mixture of two types of Fluorinert (CF70:CF77 = 1:1). Such a Teflon capsule was placed in a high-pressure clamp cell made of a Ti-Cu alloy, which has very low magnetic susceptibility. Nevertheless, the measured data were corrected for the pressure-cell signal. The hydrostatic pressure up to 1.2 GPa applied on the sample at low temperatures

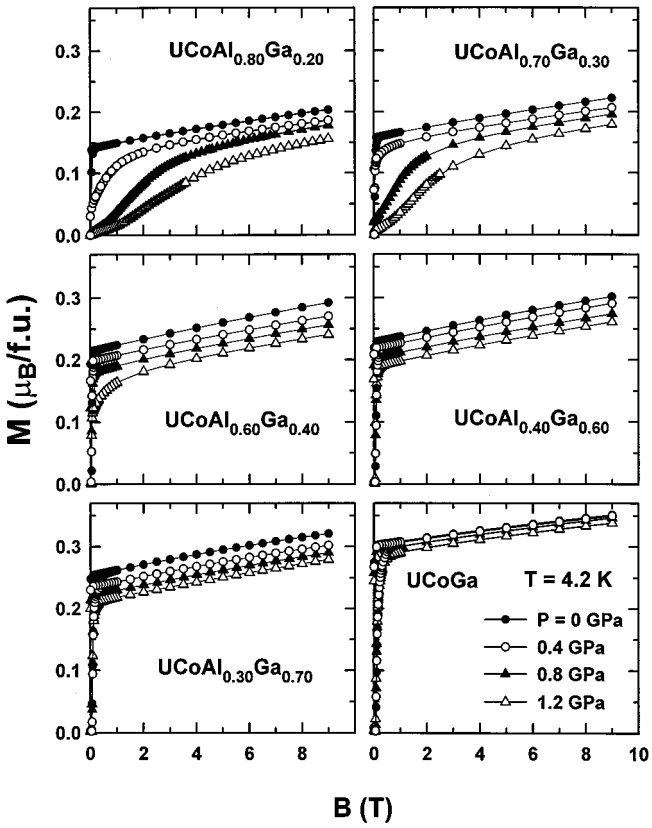

FIG. 2. Magnetization isotherms at 4.2 K of the $UCoAl_{1-x}Ga_x$ compounds measured on isotropic polycrystals at different external pressures.

was calibrated by measuring the Meissner effect of Pb, for which the pressure dependence of the superconducting transition temperature is known to high accuracy.

III. RESULTS AND DISCUSSION

In Fig. 2 we present a pressure-induced evolution of magnetization isotherms at 4.2 K for all studied compounds. One can see that ferromagnetism in compounds with $x=0.20$ and 0.30 is easily destabilized in available pressures. The process consists of a gradual suppression of the spontaneous moment accompanied by recovery of the S shape (UCoAl-like type) of a magnetization curve, which manifests the pressure-induced reentrant metamagnets. Magnetization curves for $UCoAl_{0.80}Ga_{0.20}$ and $UCoAl_{0.70}Ga_{0.30}$ samples at 4.2 K measured at elevated pressures are shown in Fig. 3 in comparison with the ambient pressure M vs B curves of UCoAl. The interplay of opposite pressure and alloying effects in this system is well documented by the coinciding M vs B curves for $UCoAl_{0.80}Ga_{0.20}$ and $UCoAl_{0.70}Ga_{0.30}$ samples measured at 0.8 and 1.2 GPa, respectively. This means that in these concentrations and pressures the increase of the Ga concentration by 0.1 yields an effect that can be roughly compensated by the increase of the pressure by 0.4 GPa.

In this context it is worth mentioning that ferromagnetism can also be induced by UCoAl by initial dilution of the U sublattice with Y. In this case, the onset of ferromagnetism may be attributed to the observed clear lattice expansion,[13] which is, however, not the case of Ga substitutions for Al

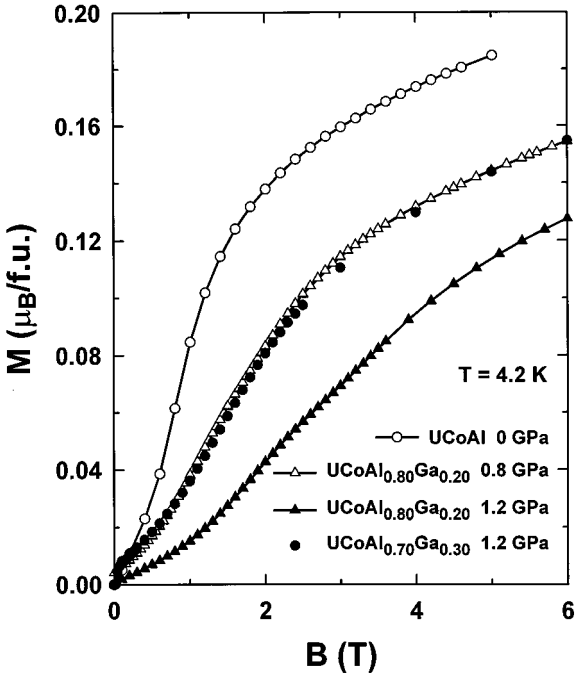

FIG. 3. Magnetization curves at 4.2 K of $UCoAl_{0.80}Ga_{0.20}$ and $UCoAl_{0.70}Ga_{0.30}$ at high pressure in comparison with the ambient-pressure behavior of UCoAl.

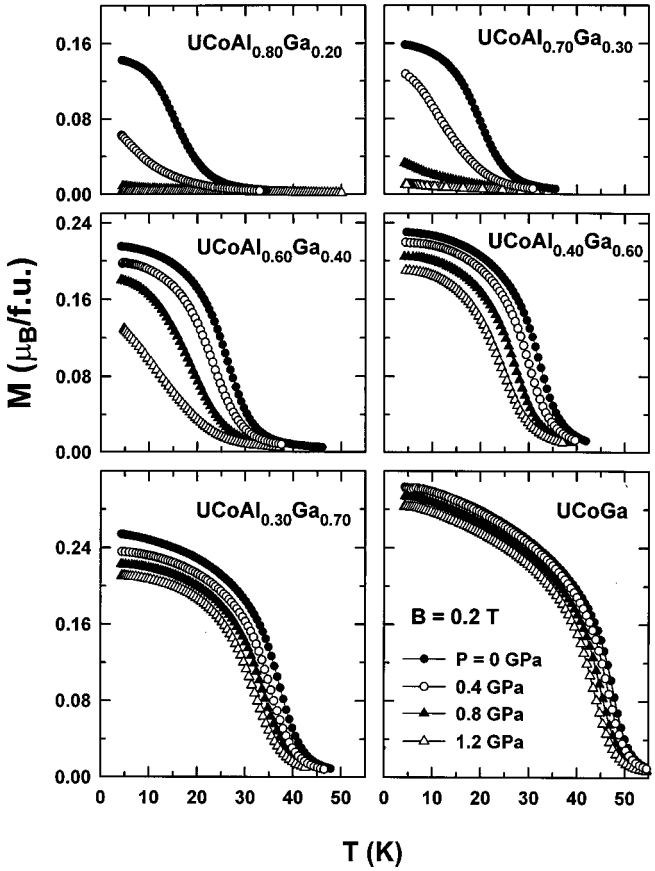

FIG. 4. Temperature dependencies of magnetization in a field of 0.2 T of the $UCoAl_{1-x}Ga_x$ compounds measured on isotropic polycrystals at different external pressures.

that lead even to slight shrinkage of the unit cell in the $UCoAl_{1-x}Ga_x$ system (Fig. 1). This means that in the latter compounds a considerable variation of electronic structure rather than the lattice-volume effect should be considered as the mechanisms responsible for the onset of ferromagnetism. This apparently points to the different roles of the $5f$(U)-$3p$(Al) and $5f$(U)-$4p$(Ga) hybridization, respectively.

Excursion to higher Ga concentrations reveals considerably less spectacular pressure effects, although some modification of the magnetization curve towards a reentrant metamagnetism is still seen on the magnetization curve for $UCoAl_{0.60}Ga_{0.40}$ in 1.2 GPa. This suggests a collapse of ferromagnetism also in this material at pressures higher than available in the present experiment.

Similar to the pressure-induced evolution of the 4.2-K magnetization curves, the pressure effects on temperature dependencies of the low-field magnetization (Fig. 4) are dramatic in compounds with lower Ga contents, whereas for concentrations $x \geqslant 0.40$ only gradual reduction of the magnetization and the Curie temperature is observed. In cases of $UCoAl_{0.80}Ga_{0.20}$ and $UCoAl_{0.70}Ga_{0.30}$, one again can see the collapse of ferromagnetism in pressures above 0.8 and 1.2 GPa, respectively, whereas the development for $UCoAl_{0.60}Ga_{0.40}$ between 0.8 and 1.2 GPa indicates that we can observe the loss of ferromagnetism if pressures above 1.2 GPa were available at our experiments. The fact that the pressure-induced low-temperature state in $UCoAl_{0.80}Ga_{0.20}$ and $UCoAl_{0.70}Ga_{0.30}$ is a state of the UCoAl type is documented by the detailed plots in Fig. 5 together with the $\chi(T)$ curve measured on UCoAl at ambient pressure, for comparison. Note that for a UCoAl single crystal we observe a clear maximum on the $\chi(T)$ curve measured in fields along the c axis (inset of Fig. 5), whereas only a monotonous Curie-Weiss–like (with large negative Θ_p) behavior is characteristic for the susceptibility in fields applied within the basal plane. On a polycrystalline sample then a superposition of these two temperature dependencies of the susceptibility is expected, yielding a bump on an otherwise hyperbolic $\chi(T)$ dependence. This bump is gradually suppressed and shifted to lower temperatures. The close relation between the low-temperature metamagnetism in external fields and maximum on the $\chi(T)$ curve is predicted by theory[3] and it is demonstrated also by the UCoAl case, in which anisotropic spin fluctuations should be considered in the theoretical approach.[5] This feature of the $\chi(T)$ curve reappears also in $UCoAl_{0.80}Ga_{0.20}$ and $UCoAl_{0.70}Ga_{0.30}$ under a sufficient pressure at which we also observe reentrant metamagnetism (Fig. 3). The strong low-temperature upturn in the $\chi(T)$ dependence (Fig. 5) reflects a small ferromagnetic contribution gradually suppressed with increasing pressure. The upturn is almost completely removed in $UCoAl_{0.80}Ga_{0.20}$ at 1.2 GPa and the $\chi(T)$ curve becomes qualitatively similar to that of a UCoAl single crystal (see the inset in Fig. 5).

Pressure dependencies of the spontaneous magnetic moment μ_s and the Curie temperature T_C in $UCoAl_{1-x}Ga_x$ are presented in Fig. 6. Supposing that the strong uniaxial anisotropy of parent compounds persists over the whole

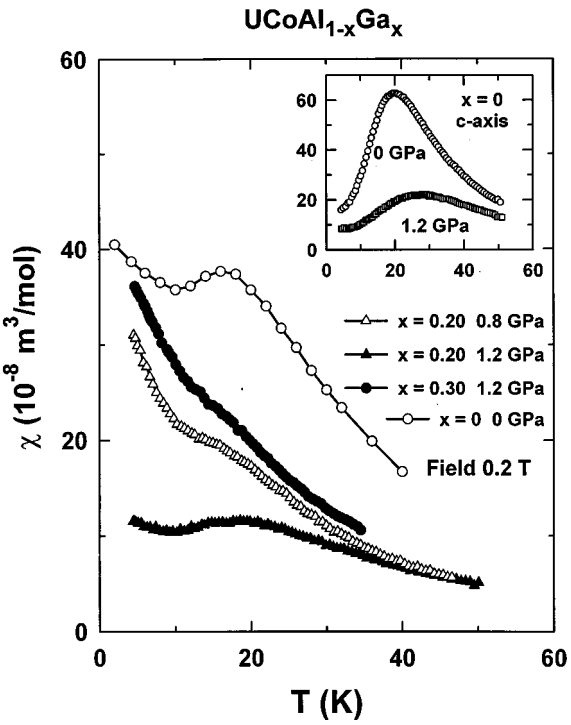

FIG. 5. Temperature dependencies of magnetic susceptibility of $UCoAl_{0.80}Ga_{0.20}$ and $UCoAl_{0.70}Ga_{0.30}$ at high pressure in comparison with the ambient-pressure behavior of UCoAl. The inset shows results for the UCoAl single crystal along the *c* axis at ambient and high pressure (Ref. 5).

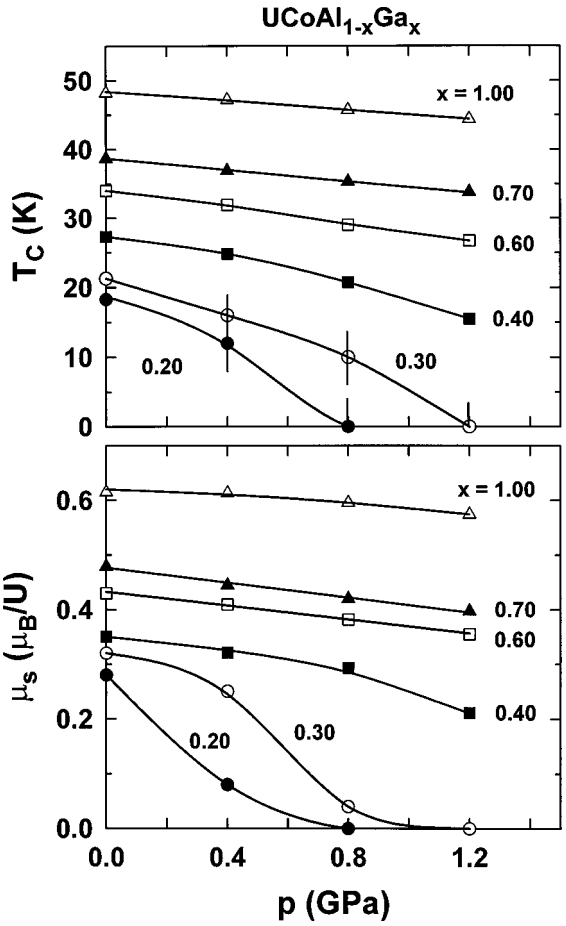

FIG. 6. Pressure dependencies of spontaneous magnetic moment μ_s and Curie temperature T_C in $UCoAl_{1-x}Ga_x$. Note that the values of μ_s are found by multiplying the values obtained from random-powder samples by a factor of 2 and correspond to those of single crystals measured along the *c* axis.

$UCoAl_{1-x}Ga_x$ system, we have calculated the values of μ_s displayed in Fig. 6 and shown in Table I by multiplying the values obtained from random-powder samples by a factor of 2. The displayed data thus represent hypothetical values, which would be measured along the easy magnetization axis on a single crystal. The value $\mu_s = 0.62\,\mu_B$ obtained in this way for UCoGa is in very good agreement with real single-crystal data,[9,10] which justifies our procedure. Owing to a nonconventional temperature dependence of the magnetic moment for compounds with $x \leqslant 0.4$ under pressure (Fig. 4), the appropriate values of T_C are determined with a larger error (up to ± 4 K, see Fig. 6) than usual (± 0.5 K).

The concentration dependencies of pressure derivatives of absolute ($d\mu_s/dp$ and dT_C/dp) and relative ($d \ln \mu_s/dp$ and $d \ln T_C/dp$) values of the spontaneous moment and the Curie temperature are displayed in Fig. 7. As can be seen in Fig. 6, the pressure dependencies of both μ_s and T_C are linear for $x > 0.4$ and nonlinear for lower Ga content. The data presented in Fig. 7 correspond to linear approximations of the low-pressure parts of the μ_s vs p and T_C vs p plots. In this figure we show also pressure derivatives of magnetic moment $d\mu/dp$ and $d \ln \mu/dp$ in a field of 8 T. For UCoAl, the results obtained on a single crystal along the *c* axis[5] are included. One can see a drastic difference between the pressure behavior of the spontaneous and the field-induced moment for $x \leqslant 0.4$. Whereas the spontaneous moment in this concentration range is extremely sensitive to the external pressure, the field-induced moment is much more stable. Its

TABLE I. Curie temperature, spontaneous moment, and relevant pressure coefficients for $UCoAl_{1-x}Ga_x$ in comparison with some other ferromagnetic U*TX* compounds (Ref. 16).

Compound	$T_C(0)$ (K)	dT_C/dp (K GPa^{-1})	$d \ln T_C/dp$ (GPa^{-1})	μ_0(4.2 K) (μ_B/f.u.)	$d\mu_0/dp$ (μ_B GPa^{-1})	$d \ln \mu_0/dp$ (GPa^{-1})
$UCoAl_{0.8}Ga_{0.2}$	18	−16	−0.86	0.285	−0.5	−1.8
$UCoAl_{0.6}Ga_{0.4}$	27	−8.3	−0.30	0.35	−0.075	−0.21
$UCoAl_{0.4}Ga_{0.6}$	34	−6.1	−0.18	0.43	−0.07	−0.16
UCoGa	48	−3.2	−0.066	0.62	−0.04	−0.06
URuSn	55	−3.4	−0.062	1.1		
URhAl	28	−0.3	−0.01	0.94		

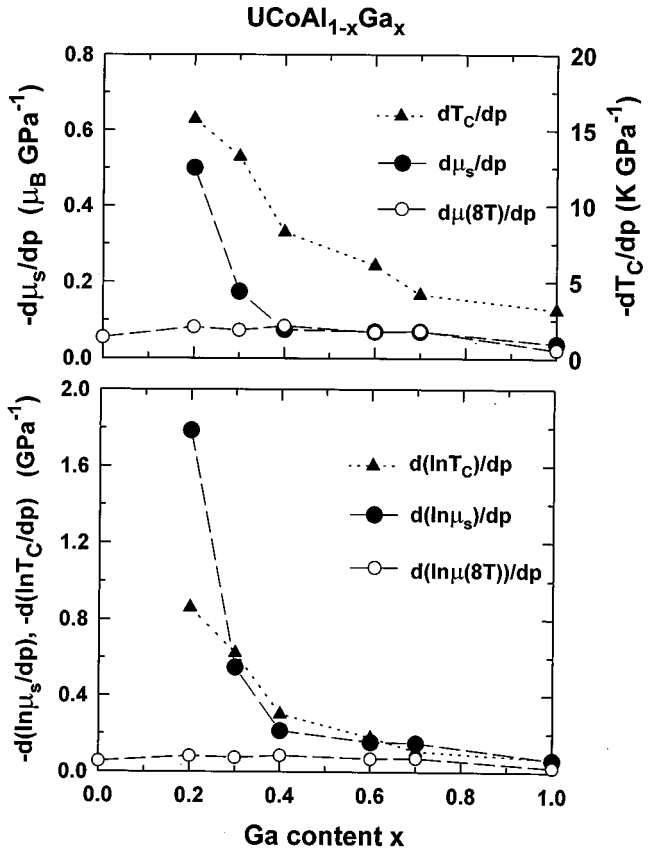

FIG. 7. Concentration dependencies of pressure derivatives of absolute (dT_C/dp, $d\mu_s/dp$, and $d\mu/dp$) and relative ($d\ln T_C/dp$, $d\ln\mu_s/dp$, and $d\ln\mu/dp$) values of Curie temperature, spontaneous magnetic moment, and magnetic moment in 8 T.

pressure derivatives depend only slightly on the Ga content. Therefore, we can attribute the anomalous pressure sensitivity of the spontaneous moment in compounds from the range of the onset of ferromagnetism not only to the instability of magnetic moment itself, but probably mainly to strong suppression of coupling between the moments that is reflected in very high values of $d\ln T_C/dp$ (see Table I).

The obtained pressure coefficients $d\ln T_C/dp$ (and $d\ln\mu_0/dp$) for $UCoAl_{0.8}Ga_{0.2}$ are not only very high compared to the other ferromagnetic $UCoAl_{1-x}Ga_x$ compounds, but they are also more than an order of magnitude larger than observed for the so far considered typical itinerant $5f$ electron ferromagnet UNi_2.[14,15]

To our surprise, we did not find any special feature in the concentration dependence of pressure derivatives of the magnetization in the vicinity of $x=0.60-0.70$, where a pronounced drop in the electronic specific-heat coefficient γ occurs.[8]

Results of this study demonstrate evolution of magnetism in the $UCoAl_{1-x}Ga_x$ compounds, in which ferromagnetism has been achieved by appropriate Ga doping. Application of a sufficient external hydrostatic pressure in lower Ga-content compounds yields reappearance of the UCoAl-type metamagnetism with main attributes of band metamagnets predicted by theory (the mutually related *S* shape of the magnetization curve and maximum in the temperature dependence of the susceptibility).[3,5] These results point to the sensitivity of principal magnetic parameters of UCoAl-based compounds to interatomic-distance variation involving both the size of U magnetic moments and exchange interactions. Lack of knowledge about the linear compressibilities of these compounds prevents us, however, from making more specific conclusions in this problem. Studies of pressure effects on lattice parameters in these materials are highly desirable.

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