Localization of 5f-electrons and pressure effects on magnetism in U intermetallics in the light of spin-fluctuation theory

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Abstract
UCoGa and URhGa, two isostructural compounds show opposite signs of the initial response of Curie temperature to applied hydrostatic pressure. To determine the physical origin of this contradiction the magnetization data measured with respect to temperature, magnetic field and hydrostatic pressure were analyzed in the framework of the Takahashi’s spin-fluctuation theory. The parameters \( T_0 \) and \( T_A \) characterizing the distribution widths of the spin-fluctuation spectrum in the energy and wave vector space, respectively, and \( T_C/T_0 \), the degree of the 5f-electron localization have been determined. Examination of available experimental data for the other UTX (\( T = \) a transition metal, \( X = \) Al, Ga) ferromagnets having the ZrNiAl-type structure revealed some correlations between the degree of the 5f-electron localization represented by the spin-fluctuation parameters and the response of Curie-temperature on the applied pressure. These observations may be applied more generally to describe the localization and magnetic behaviors of the majority of the uranium ferromagnetic compounds.

Introduction
Nowadays, quantum criticality is a heavily studied phenomenon in pure crystalline materials. In most cases, hydrostatic pressure is used to suppress magnetic ordering and to reach the desired quantum-critical behavior at finite temperatures. In the present study, we focus on a group of compounds from the UTX family (\( T = \) transition metal, \( X = \) p-metal) crystallizing in the hexagonal ZrNiAl structure. Many of these compounds are ferromagnetic with a relatively large span of Curie temperatures and magnitudes of ordered moments [1] and may therefore be used to study discontinuous phase transitions with variable parameters of magnetic order, yet with a fixed crystal structure. In several of these compounds the presence of a discontinuous phase diagram has been recently confirmed (e.g. UCoAl [2,3], URhAl [4], UCoGa [5]). On the other hand, two members of this group, UPtAl [6] and URhGa [7], respectively, show an initial (in the range of several GPa) increase of \( T_C \) with increasing pressure. It is therefore desirable to be able to predict the pressure behavior of \( T_C \) in these compounds.

In this paper, Takahashi’s spin-fluctuation theory (TSFT) [8] is used to determine if an increasing \( T_C \) with increasing pressure can be expected. In this theory, the total amplitude of the local spin fluctuations (SF) is constant as a function of temperature. This enables one to determine the value of \( F_1 \), the mode-mode coupling term as the coefficient of the \( M^4 \) term in the Landau expansion of the free energy

\[
F_m(M) = F_m(0) + \frac{1}{2(g\mu_B)^2\chi}M^2 + \frac{F_1}{4(g\mu_B)^4N_0^2}M^4,
\]

and the values of \( T_0 \) and \( T_A \), which represent the distribution widths of the SF spectrum in energy and wave vector space, respectively.
\[
\frac{T_C}{T_0}^{5/6} = \frac{M_s^2}{5g^2C_{4/3}} \left(\frac{15cF_1}{2T_C}\right)^{1/2}, \quad (2)
\]
\[
\frac{T_C}{T_A}^{5/3} = \frac{M_s^2}{5g^2C_{4/3}} \left(\frac{2T_C}{15cF_1}\right)^{1/3}, \quad (3)
\]

where \(g\) is the gyro-magnetic ratio, \(\mu_B\) is the Bohr's magneton and \(N_0\) is the Avogadro number, \(M_s\) is the spontaneous magnetic moment, \(C_{4/3}\) is constant (= 1.006089 \cdots) and \(c = \frac{1}{2}\). The value of \(F_1\) is determined from the Curie temperature and the slope of the Arrott plot \(M^2 vs M/H\) at low temperatures [8]. The ratio \(T_C/T_0\) corresponds to the degree of localization of the electrons responsible for the magnetization and ranges from \(T_C/T_0 = 1\) for the entirely localized case to \(T_C/T_0 \to 0\) for completely delocalized [8].

The compounds targeted by the study are UCoGa, with \(T_C = 48\) K [9,10] and \(T_C\) decreasing with applied pressure [5], and URhGa with \(T_C = 41\) K [10] and \(T_C\) increasing with pressures up to 6 GPa [7]. The analysis of magnetization data observed at ambient pressure reveals a clear difference of the corresponding \(F_1\), \(T_0\), \(T_A\) and \(T_C/T_0\) values obtained for the two \(UTX\) compounds. A considerably higher degree of 5f-electron localization (higher \(T_C/T_0\)) in conjunction with the narrower SF spectrum both in energy and wave-vector space (smaller \(T_0\) and \(T_A\)) have been documented for URhGa in comparison with UCoGa. The results of the analysis of pressure induced changes of \(F_1\), \(T_0\), \(T_A\) and \(T_C/T_0\) corroborate the proposed scenario of \(dT_C/dP > 0\) for URhGa in contrast to \(dT_C/dP < 0\) for UCoGa.

**Experimental**

Single crystals of UCoGa and URhGa were prepared by the Czochralski method using a tri-arc furnace. For UCoGa, details of the single-crystal preparation and annealing are presented elsewhere [11]. URhGa was grown with a pulling speed of 12 mm/hr. The ingot was wrapped in tantalum foil and annealed at 900 °C in an evacuated quartz tube. Magnetization measurements at ambient and hydrostatic pressures were performed in a MPMS XL 7T magnetometer (Quantum Design). Since the \(UTX\) compounds crystallizing in the hexagonal ZrNiAl structure exhibit huge uniaxial magnetocrystalline anisotropy with the entire magnetic moment concentrated to the \(c\)-axis [1] only the magnetization data for this field direction were measured and used for the presented analysis. For pressure experiments, a small CuBe hydrostatic cell [12] was used, with Daphne 7373 oil as a pressure medium. The superconducting transition of Pb was used to determine the pressure in the cell at low temperatures.

**Results and Discussion**

The temperature dependencies of the magnetization of UCoGa and URhGa measured in a low applied field (0.1 T) at various pressures are shown in Figs. 1 and 2, respectively. The values of Curie temperature \(T_C\) were estimated as the temperature of the inflection point of these thermomagnetic curves. For UCoGa, \(T_C\) decreases while for URhGa \(T_C\) increases with increasing pressure in agreement with earlier high pressure studies [5,7]. The phase transition in both compounds at ambient pressure is continuous (a second order transition).
Fig. 1: Temperature dependence of the magnetization of UCoGa at different pressures, in an applied field of 0.1 T.

The magnetization isotherms of UCoGa and URhGa were measured at 1.8 K, at the same pressures as the corresponding temperature dependencies of thermomagnetic curves (Fig. 3).

The values of spontaneous magnetization ($M_s$) were obtained by extrapolating the parts (above 1 T in order to avoid effects related to domains and superconducting phase of Pb) of magnetization curves to zero magnetic field. The $M_s$ values obtained for UCoGa and URhGa at different pressures are listed in Table 1. In the case of UCoGa $M_s$ is clearly decreasing with increasing pressure, whereas the $M_s$ of URhGa decreases only slightly between 0 and 0.6 GPa, and remains unchanged with higher pressures up to 1 GPa.

The Arrot plots of UCoGa and URhGa magnetization data, for all pressure points, are shown in Fig. 4. The slopes of the plots determined by linear regression and the values of $M_s$ and $T_C$ were used to determine values of the TSFT parameters $F_1$, $T_A$, $T_0$ and $T_C/T_0$ at different pressure points, and are shown in Table 1 and Fig. 5.

Fig. 2: Temperature dependence of the magnetization of URhGa at different pressures, in an applied field of 0.1
Fig. 3: Magnetization curves of UCoGa and URhGa measured at 1.8 K in magnetic fields applied along the $c$-axis at various pressures with contribution from pressure cell already subtracted. The contribution from the pressure cell was determined by comparing data in 0 GPa and ambient pressure. Lines are used as guide to eye.

To facilitate the discussion of these parameters, and their development with pressure, the complexity of the role of U 5$f$ electrons on the electronic structure and magnetism should be taken into account. The variable dual character of the 5$f$ electrons of U ions (partially localized, partially itinerant) [13–15] found in various crystallographic and chemical environments in U compounds, is reflected in the wide range of their observed magnetic behaviors. The 5$f$ wave functions are widely extended in space and allow strong 5$f$-ligand hybridization in the compounds, which destroys the original atomic character of the 5$f$ wave functions and the related magnetic moments. In the strong hybridization limit, the 5$f$ magnetic moments vanish and magnetic order is lost. The 5$f$-ligand hybridization, however, may also enforce the magnetic ordering because it mediates the indirect exchange interaction of pairs of 5$f$-electron magnetic moments born at U ions via the involved ligand [1]. In materials in which the 5$f$-ligand hybridization is not too strong, the 5$f$-moments remain stable and increasing hybridization enhances the exchange interaction and causes an increase in $T_C$. The 5$f$-ligand hybridization originates from overlaps of the U 5$f$–wave functions, with the wave functions of ligand valence-electrons and depends critically on the distances between involved ions. Thanks to compressibility, interatomic distances, and consequently the 5$f$-ligand hybridizations, can be controlled by external pressure. Isostructural families of materials, such as UTX compounds with a hexagonal ZrNiAl structure, provides a useful playground for testing the effect of ligand species and U-ligand interatomic distances on the degree of 5$f$-electron state delocalization and their implications for critical parameters of magnetic ordering while maintaining constant crystallographic symmetry. UCoGa and URhGa were selected for our study because they represent two groups of UTX compounds characterised by different signs of pressure effect on $T_C$, quantitatively expressed by $dT_C/dP$. The two compounds have similar values of Curie temperature ($T_C = 48.8$ and $41.1$ K, respectively) but the low-temperature spontaneous
magnetization $M_s = 1.16 \, \mu_B/f.u.$ of URhGa is more than double the $M_s = 0.56 \, \mu_B/f.u.$ of UCoGa. The strongly reduced U moment in UCoGa is a clear indication of a much stronger delocalization of 5f-electrons, compared to URhGa. Such a situation can be intuitively expected when we take into account the much smaller lattice parameters, in particular the $a$, in UCoGa with respect to URhGa [16]. Consequently the corresponding U-U and U-T interatomic distances within the basal plane imply a much larger 5f-5f and 5f-3d wave-function overlaps, with stronger 5f-ligand hybridization leading to much more delocalized 5f-electrons in UCoGa.

![Graph showing magnetization isotherm data for UCoGa and URhGa](image)

*Fig. 4:* The Arrot plots of magnetization isotherm data UCoGa and URhGa measured at different pressures.

From the point of view of TSFT, this situation is clearly reflected in the significantly higher magnitude of the $T_c/T_0$ ratio ($= 0.495$) obtained for URhGa compared to the $T_c/T_0 = 0.182$ obtained for UCoGa. A higher $T_c/T_0$ ratio represents more localized magnetic electrons. Consistently with better localization of the 5f electrons, the SF spectra for URhGa are much narrower both in energy and wave-vector space (smaller $T_0$ and $T_A$) than for UCoGa.

In Table 1 we can also see that the application of hydrostatic pressure on UCoGa and URhGa has a different effect on the corresponding values of $M_s$, $T_c$ and the TSFT parameters. With increasing applied pressure on UCoGa, $M_s$, $T_c$ and $T_c/T_0$ decrease rapidly. $T_0$ increases whereas $T_A$ almost doesn’t change. On the other hand, $T_c$, $T_c/T_0$ and $T_A$ of URhGa slightly increase, whilst $M_s$ and $T_0$ remain invariant.

These results fit well with the general scenario of relations between electronic structure and magnetism in U compounds, discussed above. URhGa appears in the conditions of moderate hybridization when a pressure-induced increase of hybridization increases the exchange of an interaction leading to an increase of $T_c$ without visible effect on $M_s$. On the contrary, UCoGa is in a strong hybridization mode, where a significant suppression of the U magnetic moments due to the increasing pressure prevails over the increased integration integral, so that the $T_c$ and $T_c/T_0$ decrease rapidly with increasing pressure. From the point of view of TSFT, a decrease of $T_c/T_0$ means an increasing itinerancy of 5f electrons, which leads to an extension of the SF spectrum indicated by an increasing $T_0$ value.

Investigation of URhGa to higher pressures [7] revealed $T_c$ in URhGa increases linearly ($dT_c/dP \sim 1.1 \, K/GPa$) whereas $dM_s/dP$ decreases slightly ($dM_s/dP \sim 0.02 \, \mu_B/f.u./GPa$) with
increasing pressure up to 4 GPa. In higher pressures, \( dT_c/dP \) gradually decreases and the pressure, where \( T_c \) reaches the maximum value can be expected somewhere between 6 to 9 GPa. \( M_s \) decreases much faster with increasing pressure above 4 GPa \( (dM_s/dP \sim 0.08 \mu_B/f.u./GPa) \). These are the

Table I: Experimental values of \( T_c \) and \( M_s \) with calculated values of \( F_1 \), \( T_0 \), \( T_A \) and \( T_c/T_0 \) from TSFT for UCoGa and URhGa at different pressures and \( \partial \ln T_c/\partial P \) values for \( P \rightarrow 0 \).

| UCoGa          | \( T_c \) (K) | \( M_s \) (\( \mu_B/\text{f.u.} \)) | \( F_1 \) (K) | \( T_A \) (K) | \( T_0 \) (K) | \( T_c/T_0 \) | \( \partial \ln T_c/\partial P \) |
|----------------|--------------|---------------------------------|--------------|--------------|--------------|---------------|-----------------|
| P (GPa)        |              |                                 |              |              |              |               |                 |
| 0              | 48.8         | 0.56                            | 3 060        | 1 750        | 267          | 0.182         | -0.090          |
| 0.73           | 46.0         | 0.53                            | 2 320        | 1 700        | 330          | 0.139         |                 |
| 1              | 44.5         | 0.50                            | 1 880        | 1 720        | 424          | 0.105         |                 |

| URhGa          | \( T_c \) (K) | \( M_s \) (\( \mu_B/\text{f.u.} \)) | \( F_1 \) (K) | \( T_A \) (K) | \( T_0 \) (K) | \( T_c/T_0 \) | \( \partial \ln T_c/\partial P \) |
|----------------|--------------|---------------------------------|--------------|--------------|--------------|---------------|-----------------|
| P (GPa)        |              |                                 |              |              |              |               |                 |
| 0              | 41.1         | 1.17                            | 741          | 480          | 83           | 0.495         | 0.037           |
| 0.6            | 42.2         | 1.16                            | 776          | 498          | 85           | 0.496         |                 |
| 0.86           | 42.6         | 1.16                            | 824          | 508          | 83           | 0.512         |                 |
| 1.12           | 42.8         | 1.16                            | 853          | 513          | 82           | 0.521         |                 |

| \( \text{UCo}_{0.98}\text{Ru}_{0.02}\text{Al} \) | \( T_c \) (K) | \( M_s \) (\( \mu_B/\text{f.u.} \)) | \( F_1 \) (K) | \( T_A \) (K) | \( T_0 \) (K) | \( T_c/T_0 \) | \( \partial \ln T_c/\partial P \) |
|------------------------------------------------|--------------|---------------------------------|--------------|--------------|--------------|---------------|-----------------|
| [17,18]       | 22.7         | 0.36                            | 2 311        | 1 540        | 274          | 0.083         | --              |
| \( \text{U} \text{Ir} \text{Al} \) | 62           | 0.960                           | 820          | 861          | 241          | 0.257         | -0.004          |
| \( \text{URh} \text{Al} \) [18–20] | 26.2         | 1.05                            | 428          | 340          | 64.5         | 0.365         | -0.003          |
| \( \text{UPt} \text{Al} \) [18,21]   | 43.5         | 1.38                            | 615          | 395          | 67.8         | 0.642         | 0.058           |

signatures that URhGa gradually moves towards the strong 5f-ligand hybridization regime where the washout of U magnetic moments dominates due to increasing itinerancy of 5f-electrons, so that \( T_c \) and also \( T_c/T_0 \) will decrease in higher pressures. In this respect, URhGa is analogous to UPtAl [21] which exhibits a higher \( T_c/T_0 \) \( (= 0.642 \) [18]), indicating a higher degree of localization of the 5f-electrons than in URhGa. UPtAl also exhibits an increasing \( T_c \) with increasing pressure \( [6,22,23] \). \( T_c \) reaches the maximum value at 6 GPa and then decreases with further increasing pressure up to \( \sim 17 \) GPa, where the ferromagnetism is suppressed.

We have included in Table 1, besides UCoGa and URhGa, several other UTX ferromagnets on which the pressure effects have also been studied. When inspecting the Table closely, one can observe a clear relation between the evolution of \( T_c/T_0 \), representing in TSFT the degree of 5f-electron localization, and the corresponding pressure effect on \( T_c \) values \( (dT_c/dP) \), throughout the whole series. We can also see that URhAl (contrary to URhGa) shows a (slightly) negative \( dT_c/dP \) already from the lowest pressures. The rate of \( T_c \) decrease accelerates with increasing pressure towards to the loss of ferromagnetism observed at a tricritical point at \( \sim 5.2 \) GPa \( [4] \) (similar to UCoGa \([5]\)). The opposite signs of \( dT_c/dP \) values observed for URhGa (positive) and URhAl (negative) demonstrate that the 5f-3p (URhAl) hybridization causes a stronger delocalization of the 5f-electrons than the 5f-4p (URhGa) hybridization.
The unique properties of UCoAl should be mentioned in this context, too. UCoAl in ambient pressure has a paramagnetic ground state. When applying magnetic fields UCoAl shows metamagnetic wings \[3,24\]. A slight negative chemical pressure accomplished by substituting, e.g. 4% of Lu for U, induces a ferromagnetic ground state \[25\]. The study of UCo(Al,Ga) solid solutions \[26\] revealed the gradual transformation from a paramagnetic ground state of UCoAl to ferromagnetism in UCoGa, with the onset of ferromagnetism around 20% Ga. Detailed investigation on single crystals of selected UCoAl\(_{1-x}\)Ga\(_x\) compositions is desirable to test the TSFT applied to the evolution of itinerancy of 5f-electron states in the vicinity of the critical Ga concentration for the onset of ferromagnetism.

![Fig. 5: Pressure dependence of degree of localization, \(T_c/T_0\), for UCoGa and URhGa](image)

**Conclusions**

The magnetization of UCoGa and URhGa has been measured as a function of temperature, magnetic field and hydrostatic pressure. The results were analyzed in the framework of Takahashi’s spin-fluctuation theory. The TSFT parameters \(T_0\) and \(T_A\) characterizing the distribution widths of the SF spectrum in the energy and wave vector space, respectively, and \(T_c/T_0\) characterizing the degree of the 5f-electron localization, have been determined for hydrostatic pressures up to 1 GPa. Examination of available experimental data for the other UTX ferromagnets having the ZrNiAl-type structure, revealed correlations between the degree of 5f-electron localization, represented by TSFT parameters, and the response of the Curie-temperature on the applied pressure, which may be more general and potentially valid for the majority of uranium ferromagnetic compounds.

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**Literature**

[1] V. Sechovsky, L. Havela, Chapter 1 Magnetism of ternary intermetallic compounds of
uranium, in: K.H.J. Buschow (Ed.), Handb. Magn. Mater., Elsevier, 1998: pp. 1–289.

[2] N. Kimura, N. Kabeya, H. Aoki, K. Ohyama, M. Maeda, H. Fujii, M. Kogure, T. Asai, T. Komatsubara, T. Yamamura, I. Satoh, Quantum critical point and unusual phase diagram in the itinerant-electron metamagnet UCoAl, Phys. Rev. B. 92 (2015) 35106.

[3] D. Aoki, T. Combie, V. Taufour, T.D. Matsuda, G. Knebel, H. Kotegawa, J. Flouquet, Ferromagnetic Quantum Critical Endpoint in UCoAl, J. Phys. Soc. Japan. 80 (2011) 94711.

[4] Y. Shimizu, D. Braithwaite, B. Salce, T. Combie, D. Aoki, E.N. Hering, S.M. Ramos, J. Flouquet, Unusual strong spin-fluctuation effects around the critical pressure of the itinerant Ising-type ferromagnet URhAl, Phys. Rev. B. 91 (2015) 125115.

[5] V. Sechovský, F. Honda, K. Prokeš, J.C. Griveau, A. V. Andreev, Z. Arnold, J. Kamarád, G. Oomi, Pressure effects on magnetism in U intermetallics: The UPtAl case, in: J. Magn. Magn. Mater., North-Holland, 2005: pp. 629–632.

[6] V. Sechovský, F. Honda, K. Prokeš, J.C. Griveau, A. V. Andreev, Z. Arnold, J. Kamarád, G. Oomi, Pressure effects on magnetism in U intermetallics: The UPtAl case, in: J. Magn. Magn. Mater., North-Holland, 2005: pp. 629–632.

[7] V. Sechovský, F. Honda, K. Prokeš, J.C. Griveau, A. V. Andreev, Z. Arnold, J. Kamarád, G. Oomi, Pressure effects on magnetism in U intermetallics: The UPtAl case, in: J. Magn. Magn. Mater., North-Holland, 2005: pp. 629–632.
[20] T. Combier, Ferromagnetic quantum criticality in the uranium-based ternary compounds URhSi, URhAl, and UCoAl, Université de Grenoble, 2014.

[21] A.V. Andreev, Y. Shiokawa, M. Tomida, Y. Homma, V. Sechovský, N.V. Mushnikov, T. Goto, Magnetic Properties of a UPtAl Single Crystal, J. Phys. Soc. Japan. 68 (1999) 2426–2432.

[22] A. V Andreev, J. Kamarad, F. Honda, G. Oomi, V. Sechovsky, Y. Shiokawa, Magnetoelasticity of UPtAl, J. Alloys Compd. 314 (2001) 51–55.

[23] A. V Andreev, M. Diviš, P. Javorský, K. Prokeš, V. Sechovský, J. Kuneš, Y. Shiokawa, Electronic structure and magnetism in UPtAl, Phys. Rev. B. 64 (2001) 144408.

[24] A. V Andreev, M.I. Bartashevich, T. Goto, K. Kamishima, L. Havela, V. Sechovský, Effects of external pressure on the 5f-band metamagnetism in UCoAl, Phys. Rev. B. 55 (1997) 5847–5850.

[25] A. V Andreev, V. Sechovsky, D. Rafaja, L. Dobiasova, Y. Homma, Y. Shiokawa, Onset of ferromagnetism in the 5f-band metamagnet UCoAl upon partial dilution of the U sublattice, J. Alloys Compd. 307 (2000) 77–81.

[26] A. V Andreev, N. V Mushnikov, T. Goto, V. Sechovsky, Alloying and pressure-induced transitions between 5f-band metamagnetism and ferromagnetism, Phys. Rev. B. 60 (1999) 1122–1126.