Evolution of ferromagnetic and nFL states with doping: the case of Ru doped UCoGe

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We report on evolution of ferromagnetism (FM) and non-Fermi liquid (nFL) state in the Ru doped ferromagnetic superconductor UCoGe. We have detected that Ru substitution on the Co site in the UCoGe leads to an initial sharp increase of the Curie temperature up to the maximum of \( T_C = 8.6 \) K for \( x \approx 0.1 \) accompanied by spontaneous magnetic moment enhancement. On the other hand the superconducting state vanishes already by 3% of the Ru. Further increase of the Ru content beyond \( x \approx 0.1 \) leads to the suppression of both, \( T_C \) and the spontaneous magnetic moment, creating a well-developed ferromagnetic dome in the \( T - x \) phase diagram. Concentration dependence of the critical exponents of the electronic resistivity and heat capacity together with the scaling of \( T_C \) has signs of the non-Fermi liquid behavior which suggests presence of the quantum critical point (QCP) near the critical concentration \( x \approx 0.3 \) where the ordering temperature is suppressed to zero. Detailed analysis of the critical exponents assigns the quantum phase transition most likely as a continuous Hertz-Millis type. We discuss the ferromagnetism development on the basis of band structure evolution. We support the scenario by results of electronic structure calculations and employment of the simplified periodic Anderson model.

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I. INTRODUCTION

The phenomena emerging near to the quantum critical points (QCP) belong to the most intensively studied topics of the condensed matter physics because research in this field has serious impacts on development of the new theoretical approaches for electron correlations in the materials. The research in this field is in continuous confrontation with the new coming materials carrying completely novel properties. Such intriguing materials are recently discovered uranium ferromagnetic superconductors (FM SC). This fascinating group has only three members – UGe\(_2\), URhGe and UCoGe. Superconductivity and itinerant ferromagnetism are carried by the same uranium 5\( f \) electrons. It is a big novelty distinguishing them from previously reported ones like ZrZn\(_2\) or UGe\(_2\), the first discovered case, is a model example of the superconductivity (SC) induced by external pressure. The SC appears and reaches its maximum on a boundary between the two FM phases under the high pressure. URhGe and UCoGe are ambient pressure FM SC where both phenomena naturally coexist. Lot of scientific effort in both theoretical and experimental field has been already spent to understand this mutual coexistence of FM and SC. The ferromagnetic spin fluctuations which appear in the vicinity of the QCPs inducing unconventional spin triplet SC state have been considered as the main essence of the problem. QCP can be principally reached when a (magnetic) ordering temperature is suppressed to 0 K by changing of some external non-thermal control parameter such as pressure, magnetic field or chemical doping. Quantum phase transitions (QPTs) were experimentally studied for a broad spectrum of the materials like high-\( T_C \) superconductors, ordinary metal or heavy-fermion metal. As the prominent examples one should mention CeCu\(_{6-x}\)Au\(_x\) with the antiferromagnetic quantum critical point (AF QCP) induced by chemical doping and YbRh\(_2\)Si\(_2\) where AF QCP is achieved by applying external magnetic field. In all these cases a second-order transition is reported showing continuous character. Nevertheless a ferromagnetic order in the compounds like the itinerant electron ferromagnets MnS\(_2\) or UGe\(_2\) is suppressed to the zero temperature by external pressure showing signs of a first-order transition. It has to be mentioned that these first-order phase transitions should not deserve to be marked as the QPTs according to the continuity requirement. However, such QPTs have to be treated as essentially different to the classical transitions which take place at nonzero temperatures. Thus discontinuous QPTs should be also taken into account and can in principle contribute to the investigation of the novel phase.

UCoGe, the subject of our research, is unique in the group of FM SC due to the much lower energy scale on which the magnetism appears. Curie temperature for UCoGe is only 3 K and together with the tiny spontaneous magnetic moment of 0.03 \( \mu_B \) indicates that UCoGe is close to a ferromagnetic instability. It has been observed, however, that the Ru and Fe substitution for Co stabilizes the ferromagnetic state rapidly, despite URuGe and UF\(_2\)Ge are paramagnetic down to the lowest temperatures. Similar increase of \( T_C \) was reported also in the case of Co and Ru doped URhGe. In addition, it was experimentally proved that the non-Fermi liquid state develops on the boundary of the FM dome. It is evident that the region around the Co and Rh in the TiNiSi-type UGe\(_2\) compounds (\( T = \) transition metal) offers unique conditions for the quantum phase transitions
studies. This observation motivated us to study the development of the magnetism in the UCo$_{1-x}$Ru$_x$Ge system for substitutions over a wide range of concentrations searching for the region of the inevitable disappearance of ferromagnetism where one may expect a ferromagnetic quantum critical point (FM QCP). We would like to test the type of this FM QCP, because the Co-Ru doping is not isoelectronic and in addition to it causes mixture of the 3d and 4d bands which significantly differentiate our work from previously done on URu$_{1-x}$Ru$_x$Ge. Influence of the substitutional disorder on development of the quantum phase phenomena will be also tested within our work. In the first stage an extensive investigation of structure, magnetization, magnetic susceptibility, specific heat and electrical resistance for numerous polycrystalline samples with various $x$ has been performed.

II. EXPERIMENTAL DETAILS

In order to study the development of the magnetic state in the UCo$_{1-x}$Ru$_x$Ge system we have primarily prepared a series of the polycrystalline samples with different concentration of the Ru for $x$ going from 0 to 0.9. All samples were prepared by arc-melting of the stoichiometric amounts of the elements (purity of Co 4N5, Ge 6N and Ru 3N5). We used the U purified by Solid State Electrotransport technique (SSE) following previous experiences with preparation of UCoGe. The arc melting process was realized under protective Ar (6N purity) atmosphere on a water cooled Cu crucible. Each sample was three times turned upside down and subsequently re-melted in order to achieve the best homogeneity. No sign of evaporation was observed during the melting. Resulting masses of our samples were typically 2.5 g. All samples were separately wrapped into a Ta foil (99.99%) and sealed in a quartz tube under the vacuum of $1 \cdot 10^{-6}$ mbar and subsequently annealed at 885 °C for 14 days and then slowly cooled down to room temperature to avoid creation of the internal stresses. Each sample was characterized by X-ray powder diffraction (XRPD) at room temperature on a Bruker D8 Advance diffractometer. The obtained data were evaluated by standard Rietveld technique using FullProf/WinPlotr software with respect to the previously published crystallographic data of the UCoGe and URuGe compound. Chemical composition of our samples was verified by scanning electron microscope (SEM) Tescan Mira I LMH equipped by an energy dispersive X-ray detector (EDX) Bruker AXS. Samples were afterward properly shaped for individual measurements with a fine wire saw to prevent additional stresses. Bar-shaped samples ($1 \times 0.5 \times 4$ mm$^3$) were used for the low temperature resistivity measurements performed on a PPMS14T (Quantum Design) with the $^3$He insert down to 350 mK. Heat capacity measurements were performed on the thin plates ($2 \times 2 \times 0.2$ mm$^3$) using relaxation method on the PPMS9T and PPMS14T devices using the same $^3$He insert. Magnetization measurements were done on the roughly cubic samples ($2 \times 2 \times 2$ mm$^3$) in a MPMS7T device. The density of states calculations were performed on the basis of the density-functional theory (DFT) within the local-spin-density approximation (LSDA) and the generalized gradient approximation (GGA) We used the full-potential augmented-plane-wave together with the local-orbitals method (APW+lo) as a part of the latest version (WIEN2k) of the original WIEN code for these calculations.

III. RESULTS

UCoGe and URuGe both possess the orthorhombic TiNiSi structure (space group Pnma) with the cell parameters $a = 6.852$ Å, $b = 4.208$ Å, $c = 7.226$ Å and $a = 6.678$ Å, $b = 4.359$ Å, $c = 7.539$ Å, respectively. Thus the unit cell volume of the ferromagnetic UCoGe is smaller ($V = 208.3$ Å$^3$) of about 5% than the URuGe compound ($V = 219.5$ Å$^3$). XRPD patterns confirmed orthorhombic TiNiSi-type structure in the whole series of the doped materials. Typically all reflections could be assigned to the expected TiNiSi structure. One representative XRPD pattern is displayed in Fig. 1

The evaluated lattice parameters of the Ru doped samples are shown with respect to increasing Ru concentration in Fig. 2. The concentration dependence of all three lattice parameters and also the unit cell volume is linear, i.e. obey the Vegard’s law (see Table I).

While the $b$ and $c$ lattice parameters increase with the increasing $x$ the lattice parameter $a$ simultaneously decreases. The volume expansion seems to be reflecting the increase of the covalent radii from the Co (126 pm) to Ru (146 pm). Refinement of the diffraction patterns

![FIG. 1. (Color online) - Representative XRPD pattern of the UCo$_{0.8}$Ru$_{0.2}$Ge compound. Red points refers to measured intensities, black bold line is calculated pattern, blue thin line is difference and vertical bars are positions of the Bragg peaks.](image-url)
TABLE I. Unit cell parameters and volume as obtained from the refinement of the X-ray powder diffraction patterns.

| x    | a (Å)     | b (Å)     | c (Å)     | V (Å³)    |
|------|-----------|-----------|-----------|-----------|
| 0.10 | 6.8344    | 4.2188    | 7.2717    | 209.6671  |
| 0.20 | 6.8216    | 4.2267    | 7.3048    | 210.6173  |
| 0.21 | 6.8204    | 4.2261    | 7.3079    | 210.6840  |
| 0.22 | 6.8189    | 4.2279    | 7.3085    | 210.6325  |
| 0.23 | 6.8178    | 4.2280    | 7.3229    | 211.2003  |
| 0.24 | 6.8189    | 4.2320    | 7.3347    | 211.2355  |
| 0.25 | 6.8203    | 4.2363    | 7.3314    | 211.8247  |
| 0.26 | 6.8205    | 4.2390    | 7.3389    | 211.8711  |
| 0.27 | 6.8077    | 4.2373    | 7.3413    | 211.7662  |
| 0.28 | 6.7880    | 4.2454    | 7.3704    | 212.3984  |
| 0.29 | 6.7709    | 4.2577    | 7.4046    | 213.4669  |
| 0.30 | 6.7522    | 4.2710    | 7.4416    | 214.6050  |
| 0.31 | 6.7336    | 4.2868    | 7.4741    | 215.7451  |
| 0.32 | 6.7137    | 4.3015    | 7.5041    | 216.7105  |
| 0.33 | 6.6909    | 4.3212    | 7.5290    | 217.6849  |

FIG. 2. (Color online) - Concentration dependence of the lattice parameters and unit cell volume in UCo$_{1-x}$Ru$_x$Ge system. The lines serve as guides for the eye.

showed, that the Ru atoms really substitute only Co atoms on their sites. If we implemented the site Co(Ru)-Ge mixing the resulting $R$ factor of such fit was always worse.

The XRPD patterns also allowed us to plot evolution of the $d_{U-U}$ distance. Although the unit cell volume expands towards Ru the $d_{U-U}$ distance contracts (see Fig. 3). It is not surprising result considering that the shortest $d_{U-U}$ is along the crystallographic axis $a$. It is only the one which contracts with the increasing Ru content.

We have performed series of the magnetization and AC susceptibility measurements on samples over a wide Ru doping range. In low Ru concentrations $T_C$ steeply increases with increasing $x$ in agreement with results presented in previous work. This trend terminates at $x_{\text{max}} \approx 0.1$ where the ordering temperature reaches its maximum $T_C, \text{max} \approx 8.6$ K, which is almost three times higher in comparison to the $T_C = 3$ K of the parent compound and it compares to the value found by Huang et al. in the case of Fe doping. Further increase of the substituted Ru atoms on the Co site yields steady suppression of the ferromagnetic phase when the $T_C$ drops to zero near critical concentration $x_{\text{cr}} \approx 0.3$ (see Fig. 12). The concentration evolution of $T_C$ trend is followed by simultaneous development of the spontaneous moment. The magnetization curves clearly show rapid increase of the spontaneous moment up to $\sim 0.1 \mu_B/\text{f.u.}$ for $x \approx 0.1$ which is followed by a steady decrease with further increasing $x$. We have estimated the spontaneous magnetic moment $\mu_{\text{spont}}$ from the magnetization curves $M(H)$ measured at 1.85 K by extrapolating the magnetic moment from the high magnetic fields to zero (see Fig. 4). The values of the spontaneous moments determined for all samples are listed in the Table II and plotted in the complex phase diagram in Fig. 12.

The $T_C$ values were determined from the Arrott plot. For this purpose we have measured magnetization curves up to the 7 T at various temperatures around expected $T_C$ for each sample. The Arrott plots were strongly nonlinear in our case. Therefore we tried to evaluate the curves by the third degree polynomial function (see modeling example in Fig. 5) in order to find the interception with the $M^2$ axis of the plot. Extrapolation of the cross-sections with $M^2$ axis for the different temperatures to the value for $M^2 = 0$ was figured out as an estimation of the final $T_C$. Example of this construction is in the inset of Fig. 5.

We certainly tried to understand the nonlinearity of the Arrott plots. Cubic dependence in the $M^2$ vs $H/M$ clearly suggests presence of a component linearly field
FIG. 4. (Color online) - Magnetization curves measured at $T = 1.85$ K for different concentrations of Ru up to the 7 T. Only representative concentrations are plotted for clarity.

TABLE II. Values of the spontaneous magnetic moment $\mu_{\text{spont}}$, $T_C$ from Arrott plot construction, from AC susceptibility, from magnetization data, specific heat and Sommerfeld gamma coefficient as determined for various concentration of Ru.

| $x$ | $\mu_{\text{spont}}$ ($\mu_B$) | $T_{C,\text{Arrott}}$ (K) | $T_{C,\text{AC}}$ (K) | $T_{C,\text{mag}}$ (K) | $T_{C,\text{Cp}}$ (K) | $\gamma$ (mJ/m²K²) |
|-----|--------------------------------|--------------------------|----------------------|----------------------|----------------------|------------------|
| 0   | 0.0300                         | -                        | -                    | -                    | -                    | -                |
| 0.01| 0.0330                         | 4.20                     | -                    | 7.50                 | -                    | -                |
| 0.05| 0.0750                         | 8.30                     | -                    | 8.60                 | -                    | -                |
| 0.10| 0.1060                         | 8.62                     | -                    | 8.60                 | 0.0861               | -                |
| 0.20| 0.0540                         | 5.70                     | -                    | 5.40                 | 5.70                 | 0.1066           |
| 0.21| 0.0580                         | 5.70                     | 5.20                 | 5.40                 | 5.90                 | 0.1100           |
| 0.22| 0.0594                         | 5.01                     | 4.70                 | 5.00                 | 5.30                 | 0.1133           |
| 0.23| 0.0568                         | 4.68                     | 4.20                 | 4.60                 | 4.30                 | 0.1152           |
| 0.24| 0.0270                         | 3.55                     | 3.50                 | 3.60                 | 3.80                 | 0.1258           |
| 0.25| 0.0300                         | 3.49                     | 3.40                 | 3.40                 | 3.30                 | 0.1333           |
| 0.26| 0.0213                         | 2.51                     | 2.80                 | 2.80                 | 3.00                 | 0.1353           |
| 0.27| 0.0223                         | 2.77                     | 2.40                 | 2.60                 | 2.80                 | 0.1435           |
| 0.28| 0.0219                         | 2.32                     | 1.90                 | 2.30                 | 2.70                 | 0.1405           |
| 0.29| 0.0077                         | -                        | 1.44                 | -                    | 1.40                 | 0.1529           |
| 0.30| 0.0013                         | -                        | -                    | -                    | -                    | 0.1598           |
| 0.40| 0.0011                         | -                        | -                    | -                    | -                    | 0.1523           |
| 0.50| 0.0001                         | -                        | -                    | -                    | -                    | 0.1490           |

dependent to the magnetization. As an evidence for this scenario stands the strong magnetic uniaxility of the system with the $c$ axis as the easy magnetization direction\cite{21}. Contribution of the hard axes ($a$ and $b$) to the field dependence of the magnetization is linear (i.e. paramagnetic). For this purpose we tried to subtract the linear term from our measured magnetization $M$ obtaining the corrected value $M^* = M - a \cdot H$. We have obtained linear isotherms for the value of the slope $a = 0.006$ in the revised Arrott plot construction. Example of this data treatment is presented on the exemplary case of the UCo$_{0.77}$Ru$_{0.23}$Ge in Fig. 5.

Temperature dependence of the magnetization follows results from the magnetization curves (see Fig. 7). Development of the spontaneous and saturated magnetic moment is also observable on the change of the shape of magnetization curves (see Fig. 4).

The values of ordering temperatures obtained from the Arrott plot analysis are in good agreement with the position of the inflection points in the $M(T)$ dependencies (measured in the external field of 10 mT) and also with the maxima of the real parts of the AC susceptibility $\chi'$.
Temperature dependences of the specific heat $C_p(T)$ at low temperatures support our results from the magnetization measurements. We have used the inflection point of the $C_p/T$ vs. $T$ anomalous as an estimation of the Curie temperatures $T_C$ due to rather broad transitions for $0.1 < x < 0.3$. These values are comparable to those derived from magnetization data. These $T_C$ values are also plotted in the Fig. 12. We subsequently subtracted the lattice contribution using the fit of the lattice specific heat as a $C_{lat}(T) = \beta T^3$. We have typically received the values of the $\beta \approx (0.52 - 0.56) \times 10^{-3} \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-4}$ i.e. the Debye temperature of 151–155 K was evaluated for each sample in the temperature interval between $T_C$ and 20 K. Figure 7 shows $f$-electron specific heat $C_m = C - C_{lat}$ plotted as $C_m/T$ vs log$T$. The anomaly at $T_C$ is clearly smeared down and shifted to lower temperatures with increasing of the Ru concentration. Finally, the specific heat shows sign of almost linear trend in the temperature region $(1 - 10)$ K for $x \approx 0.31$. We will discuss later this behavior in scenario of the nFL state development. nFL is characterized by the logarithmic dependence of the specific heat divided by temperature $C_m(T)/T = c \ln(T_0/T)$. This is expected for the concentrations in the vicinity of a QCP.

However, our data do not follow linear prediction in the whole temperature range. Nevertheless, it is very similar to the case of the UCo$_{1-x}$Fe$_x$Ge system which is claimed as exhibiting nFL behavior. Contrary to the UCo$_{1-x}$Fe$_x$Ge system a perfectly linear trend was found around critical concentration in the similar URh$_{1-x}$Ru$_x$Ge system. Origin of this effect will be discussed later.

If we calculate magnetic entropy $S_{mag}$ integrated over the temperature range from 0.7 K up to the $T_C$ for each sample we can observe steady decrease of this value from 0.13 R ln 2 for $x = 0.1$ down to the 0.006 R ln 2 at $x = 0.30$ (see Fig. 12) which is consistent with gradually disappearing itinerant magnetic moment when approaching QCP ($x \approx 0.31$). As the system approaches the critical concentration we can also observe dramatic increase of the Sommerfeld $\gamma$ coefficient ($\gamma \sim x^2$) from the former 57 mJ/mol $\cdot$ K$^2$ (Ref. 33) for the parent UCoGe up to the 160 mJ/mol $\cdot$ K$^2$ at $x = 0.3$ near $x_{cr}$ which is followed by decrease of the $\gamma$-value with increasing Ru concentration beyond $x_{cr}$. According to the prediction for the dependence of Curie temperature ($T_C$) on the value of con-
crystalline samples shows an initial increase up to the maximum at $T_0$ (see inset of the Fig. 11). An analogous effect is observed in the resistivity data measured on the UCoGe single crystal for current along the c-axis. This resistivity increase effect is most likely connected with the spin fluctuations when $T^{5/3}$ spin fluctuation theory for a weak itinerant ferromagnet is applicable at temperatures below the knee. The maximum can also well correspond with the field induced moment polarizability reported by Knafo et al. Our data measured on polycrystalline samples reveal general increasing dependence of the temperature $T_0$ on the Ru content $x$ but with no sign of a perfectly regular trend, which can be caused by polycrystalline materials. The reduced size of the effect measured on polycrystals is probably due to averaging the anisotropic resistivity. Even small sign of preferred orientation of grains in the polycrystal or its texture can dramatically change the temperature dependence of the measured electrical resistivity. Some samples exhibited well pronounced maximum at $T_0$ while the others showed rather broad plateau or even almost a common metallic features. The first case shows preferred orientation along the magnetic easy axis $c$ while the broad plateau can be sign to the orientation along one of the hard magnetization axes ($a$ or $b$). Nevertheless the overall increase of the $T_0$ corresponds to the fact that the knee is not present in the data measured on the polycrystalline samples up to the 300 K for the URuGe compound. The resulting temperature dependencies of the electrical resistivity ratios for selected polycrystalline samples are plotted in Fig. 11.

Anomalies connected with the transitions from ferromagnetic to the paramagnetic state are not so clearly visible on the polycrystalline data. Arrows in Fig. 11 show $T_C$ obtained from the analysis of the Arrott plots. $T_C$ estimated from the specific heat data are used for the samples with lower $T_C$ in Fig. 11. It is obvious, that increased Ru content dramatically changes the curvature of the low temperature part of the resistivity in the UCo$_{1-x}$Ru$_x$Ge system. We have performed fitting of the resistivity data below $T_C$ for each data set ($x = 0.21–0.30$) using formula taking into account contribution of the ferromagnetic magnon gap which was successfully used for evaluation of the resistivity data of the strongly anisotropic system. For this reason we used equation (1)

$$\rho = \rho_0 + AT^2 + C_mT\Delta \left(1 + \frac{2T}{\Delta}ight) \exp \left(-\frac{\Delta}{T}\right)$$

The size of the gap varies in the interval $\Delta \approx 0.5–5$ K. We have employed the general expression $\rho = \rho_0 + AT^n$ for temperatures above $T_C$. The inflection point was used as an upper limit for the fitting because it is always presented in measured data, due to the increasing resistivity as it approaches maximum value at $T_0$. The exponent gradually decreases as the Ru content approaches the critical concentration $x_{cr}$. The minimum value of $n \approx 1.13$ for $x = 0.31$ is close to the proposed linear tem-

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**FIG. 9.** (Color online) - Electron specific heat divided by temperature for samples with different Ru content in the logarithmic scale. Only few concentrations are plotted for clarity. Black arrows shows the position of $T_C$ for the $x = 0.10$ and $x = 0.22$ at the inflection point. Dashed line shows linear dependence of the specific heat for $x = 0.31$.

**FIG. 10.** (Color online) - Estimation of the critical concentration using the $T_C$ from the Arrott plots as the most plausible values were used for construction of the picture. Liner behavior of the $T_C$ support correctness to use the $T_C \sim (x_{cr} - x)^{3/4}$ law.
We have found common value of the RRR for polycrystalline samples with \( \rho \) state pronounced as an increase of the value of electrical resistivity for selected polycrystalline samples with higher concentration of ferromagnet. The samples with higher concentration of Ru \((x > x_{cr})\) exhibited steady recovery to the FL state pronounced as an increase of the value of exponent. 

Results of the \( \rho = \rho_0 + AT^n \) fits are plotted in the Fig. [11] and development of the exponent \( n \) is summarized in the \( T \) \( -x \) phase diagram (Fig. [12]). We have also observed quite low RRR= 1\( \times \)1 of the samples, given as a \( \rho_{300 K}/\rho_{0.4 K} \), through the whole series of polycrystalline samples with \( x > 0.2 \). It shows that the chemical doping induces remarkable disorder in the system (see Fig. [12]).

We have found common value of the RRR for polycrystalline samples of parent UCoGe between 6 and 10. We calculated the logarithmic derivative of the electrical resistivity according to the Eq. (2) in order to see direct change of the \( n \) exponent as a function of temperature

\[
  n = \frac{d \ln (\rho - \rho_0)}{d \ln T}
\]  

The results of this analysis are plotted in the phase diagram (Fig. [12]). It reveals a significant change of the exponent in the ordered region where \( n \geq 2 \) and in the higher temperatures where \( n < 2 \). Remarkable is a sharp drop of the \( n \) value near the critical concentration down to the lowest temperatures surrounded by regions of higher \( n \) (rapidly increasing on the FM side for \( x < x_{cr} \) and slower increase on the paramagnetic side). Absence of the sharp transition at the \( T_C \) for polycrystalline samples leads to the broadened region of the \( n \approx 2 \) exponent also above the Curie temperature.

We have applied the first-principles theoretical methods to better understand the changes in the electronic structure of the \( \text{UCo}_{1-x}\text{Ru}_x \text{Ge} \) system. While the density of states of the parent compound UCoGe is known \((\text{Ref. 41})\) the information about the paramagnetic \( \text{URuGe} \) was missing. Calculated total and partial DOS of the \( \text{URuGe} \) are plotted in Fig. [13].

We used the calculated \( \text{URuGe} \) band structure to apply a simple model of Silva Neto et al.\((\text{Ref. 42})\) based on the periodic Anderson model.\((\text{Ref. 43,44})\) This simplified model proposes the key role of the \( nd - 5f \) hybridization \((V_{df})\) in the non-monotonous evolution of \( T_C \) in the \( \text{URh}_{1-x}\text{Co}_x \text{Ge} \) system. They described the \( T_C \) evolution as a consequence of the broadening of the \( nd \) and \( 5f \) bands \((W_d, W_f)\) and mutual shift of their centers \((C_{Td} - C_{Uf})\) related as follow\((\text{Ref. 42})\)

\[
  V_{df} = \frac{W_d W_f}{C_{Td} - C_{Uf}}
\]

If we follow this model for the \( \text{UCo}_{1-x}\text{Ru}_x \text{Ge} \) system we can qualitatively describe the non-monotonous evolution of \( T_C \). The concentration dependence of the \( nd \) band broadness is assumed to be linear following Eq. 4

\[
  W_d (x) = W_d^{Co} (1 - x) + W_d^{Ru} (x)
\]

where \( W_d^{Co} = 6.1 \text{eV}\)(\text{Ref. 13}) and \( W_d^{Ru} = 8.7 \text{eV} \) (see Fig. [13]) and \( W_f = 0.43 \text{eV} \)(\text{Ref. 13}). Such behavior is consistent with other \( UTX \) \((T=\) transition metal, \( X = \) \( p \) element) compounds where the \( d \) band broadens while we move from the 3\text{d} to the 4\text{d} transition metals.\((\text{Ref. 13})\) Consequently the \((C_{Td} - C_{Uf}) (x) = \Delta C_{df} (x) \) deviates from the linearity

\[
  \Delta C_{df} = \Delta C_{df}^{Co} (1 - x) + \Delta C_{df}^{Ru} x + \delta' x^2 (1 - x) + \delta'' x (1 - x)^2
\]

We used the values from calculated DOSes, i.e. \( \Delta C_{df}^{Ru} = 0.65 \text{eV} \) and \( \Delta C_{df}^{Co} = 1.5 \text{eV} \)(\text{Ref. 13}) and adjustable parameters were taken as \( \delta' = 2 \cdot 10^{-5} \) and

![FIG. 11. (Color online) - Temperature dependence of the electrical resistivity for selected polycrystalline samples with gradual Ru content. Red arrows denote the \( T_C \) obtained from the Arrott plots analysis and from the heat capacity data. Solid lines are fitted by the Eq. (1). Dashed lines are fits to the Arrott plots analysis and from the heat capacity data.](image-url)
\[ \delta^{-1} = 2 \]

Such approach gives us non-monotonous dependence of the \( d - f \) hybridization term \( V_{df} \) starting with \( V_{df} (x = 0) \approx 1.73 \) for UCoGe (in agreement with Ref.\textsuperscript{43}), \( V_{df} (x = 1) \approx 5.55 \) for URuGe and \( V_{df} (x \approx 0.3) \approx 1.9 \) as estimated for the ferromagnetic QCF\textsuperscript{42}. The overall \( V_{df} (x) \) dependence starts with its decrease which causes enhancement of the density of \( f \) states at the Fermi level\textsuperscript{46}. Using usual approach for the itinerant ferromagnets we can estimate the ordering temperature as a function of the density of states at the Fermi level \( T_C \approx (IN(E_F) - 1)^{3/4} \) where \( I \) is the so called Stoner integral\textsuperscript{47}. In this outlook we can attribute the initial increase of \( T_C \) to the enhanced \( N(E_F) \). At \( x \approx 0.07 \) the \( d - f \) hybridization reaches its minimum value \( V_{df} = 1.7 \) and starts to increase for increasing \( x \). This point qualitatively agrees with the position of maximum \( T_C \) in experimental data at \( x \approx 0.1 \). As the concentration of the dopant is higher the \( d \)-band is shifted closer to the position of the \( f \)-band and the hybridization increases which is leading to the lowering of the \( f \)-DOS contribution to the density of states at the Fermi level\textsuperscript{46}. For the reason mentioned above the ordering temperature decreases and reaches zero near \( x_{cr} \approx 0.3 \).

**IV. DISCUSSION**

In general, magnetism of the uranium systems is strongly affected by the direct overlap of the \( 5f \) wave functions with subsequent delocalization of the \( 5f \) electron and consequent washout of the \( 5f \) magnetic moments. One would expect in the most simple model a continuous vanishing of the FM from UCoGe to URuGe due to the contraction of the \( d_U-U \) distance approaching Hill limit\textsuperscript{43} (Fig. 3 and Fig. 14).

But it is not valid, not only in the UCo\textsubscript{1-x}Ru\textsubscript{x}Ge system but also in many neighboring others like UCo\textsubscript{1-x}Fe\textsubscript{x}Ge\textsubscript{13} URh\textsubscript{1-x}Ru\textsubscript{x}Ge\textsubscript{13} or URh\textsubscript{1-x}Co\textsubscript{x}Ge\textsubscript{14}. The situation is more complex and \( 5f \)-ligand hybridization should be taken into account. The significant influence of the hybridization is apparent in non-monotonous development of the critical temperatures in UGe com-
FIG. 14. (Color online) - Illustrative plot showing dependence of the ordering temperature of the UTGe compounds ($T = \text{transition metal}$) on the shortest distance between two nearest uranium atoms ($d_{U-U}$). Shaded region spreads around Hill limit (3.5 Å) valid for uranium. Position of the UFeGe is exceptional because the UFeGe does not keep the TiNiSi-type structure. Information about the structure and magnetic features of the UOsGe compound is missing till today to complete and confirm the suggested trends.

... pounds when one moves from 3d to 5d or from the Fe-group to Ni-group. Thus, the explanation of the non-monotonous (dome-like) concentration dependence of the Curie temperature and ferromagnetic state seems to be controlled by the 5f ($U$)−nd ($T$) hybridization which apparently plays dominant role in these materials. The hybridization plays a dual role in magnetism: a) it can mediate an indirect exchange interaction which is promoting magnetic ordering, b) it disturbs the atomic character of the involved electron wave-functions which leads to delocalization of the 5f electron and washing out the 5f-magnetic moments.

Within this scenario we have followed the simple model dealing with the widths and positions of the nd and 5f bands described in Ref. to identify mechanism responsible for the FM behavior in UCo$_{1-x}$Ru$_x$Ge. The dome-like character of the phase diagram in the case of isoelectronic substitution in the system URh$_{1-x}$Co$_x$Ge results from the competition between the reduction of the $d-f$ hybridization caused by narrowing of the $d$ band. Co 3d band character and simultaneous approaching of the $d$ band towards the $f$ band lead to the enhancement of the hybridization. Our non-isoelectronic substitution in UCoGe of Co by Ru causes broadening of the $d$ band from 3d to the 4d transition metal-like. Together with the mutual shift of the $d$ and $f$ bands towards them itself we can qualitatively describe dome-like dependence of the ordering temperature $T_C$. UCo$_{1-x}$Ru$_x$Ge system is important confirmation of the trend. Changes in the $f-d$ hybridization varies magnetic ground state also in the analogous systems like URh$_{1-x}$Ru$_x$Ge and UCo$_{1-x}$Fe$_x$Ge.

The magnitude of the hybridization is well reflected in relation to the ZrNiAl-type UTAI compounds ($T = \text{transition metal}$), which can also originate in the different geometry of the ions. The UFeA and URuA are also paramagnets. UCoA compound is close to a ferromagnetic instability and the URhA one is a strong ferromagnet. Ferromagnetic domes also develop in the URh$_{1-x}$Ru$_x$A and UCo$_{1-x}$Fe$_x$Gex compounds. However the $T_C$s are significantly higher and the domes survive up to much higher concentrations of the nonmagnetic analogue. In the UCo$_{1-x}$Fe$_x$Gex almost up to the nonmagnetic URuAl compound. It is evident that the $d-f$ hybridization in the alloying TiNiSi-type UTGe compounds works rather as the delocalization mechanism of the 5f electrons while in the ZrNiAl-type UTAI compounds as the indirect interaction mediating stable magnetic order. Strong delocalization of the 5f electrons is reflected by strong decrease of the magnetic entropy $S_{mag}$ down to the 0.006 $\text{R} \ln 2$ for $x \approx 0.3$ points on the itinerant nature of the weak magnetism in the vicinity of the critical concentration. We would expect magnetic entropy equal to zero for an ideal itinerant ferromagnet.

We cannot also neglect the influence of the contraction of the $d_{U-U}$ distance. The original increase of the $T_C$ at the low Ru concentration contradicts the $d_{U-U}$ behavior and 5f−d hybridization seems to be the leading effect responsible for the ferromagnetism behavior. The $d_{U-U}$ interatomic distance can partly contribute to later development of the nFL and paramagnetic state in the higher concentration of the Ru because the pure compounds in AnTGe (An = actinide element, $T = \text{transition metal}$) series surprisingly fulfill the Hill behavior as was suggested in the phase diagram in Re. However, the ratio and separation of the hybridization effect from the influence of the $d_{U-U}$ cannot be carried out on the basis of our available macroscopic data.

Our results of the temperature dependence of the electrical resistivity and heat capacity show signs of the nFL behavior in the vicinity of $x_{cr}$ pointing on the possible presence of the FM QCP. We have observed drop of the $n$ exponent in the temperature dependence of resistivity ($\rho = \rho_0 + AT^n$) and almost linear dependence of the reduced heat capacity $C_m(T)/T = c \ln (T/T_0)$ at low temperatures what would be in agreement with the theoretical predictions of Millis and Herr. Another evidence for the FM QCP is rapid increase of the Sommerfeld coefficient $\gamma$ near $x_{cr}$. The proposed scenario is also sustained by scaling of the ordering temperature with control parameter itself; obeying $T_C \sim (x_{cr} - x)^{3/4}$ and giving estimation of critical concentration $x_{cr} \approx 0.31$.

Our heat capacity data follow the $C_m(T)/T = c \ln (T/T_0)$ function only in very limited region in our system in the lowest temperatures. Nevertheless, the same effect was observed weakly in the case of URh$_{1-x}$Ru$_x$Ge and in the UCo$_{1-x}$Fe$_x$Ge compounds. However, in our
UCO$_1-x$Ru$_x$Ge compound is this effect the strongest. We suppose that the effect originates from non-isoelectronic doping and mixture of the 3$d$-4$d$ bands which can cause that the nFL state is not so well developed because of the disorder effect.

Thus, we conclude that the tuning of the system to the QCP by doping brings large obstruction in the form of disorder. This effect can be neglected in the case of pressure or magnetic field driven QPT, but in our case it deserves deeper discussion. Disorder caused by doping can be one of the reasons of the lacking of SC in the proximity of these secondary QCPs including our UCO$_1-x$Ru$_x$Ge system. While SC in the UCoGe is proposed to be unconventional$^{18}$ it should be very sensitive to the impurities according to the generalized form of the Abrikosov-Gor’kov pair-breaking theory$^{50,54}$. Our phase diagram in Fig. 12 is supplemented by two data points from Ref. $^{13}$ showing how rapidly is SC lost within the system. Iron doping brings comparable results$^{50}$, while external pressure keeps SC almost untouched in wide pressure range$^{55}$. Disorder can also in some cases emulate nFL behavior$^{59}$; so interpretation of such results should always be done with the proper precaution. The effect of disorder can in principle also affect the order of the phase transition, i.e. blurring the first-order transition to the continuous second-order one. Our samples showed rather small RRR values $\sim$ 1.2 which is similar to the compounds UCO$_1-x$Fe$_x$Ge$^{19}$, URh$_{1-x}$Ru$_x$Ge$^{18}$ where transition to the FM state is proposed to be of the second-order, as well.

V. CONCLUSIONS

We have successfully prepared series of the polycrystalline samples of UCoGe doped by Ru in the wide concentration range. Ru doping leads to developments of the FM dome between $x = 0 - 0.31$ when maximum of the $T_c = 8.6$ K and spontaneous moment of $\mu_{eff} = 0.1$ $\mu$B appears at the $x \approx 0.1$. Further increase of the Ru content up to the $x = 0.31$ leads to the vanishing of the FM and critical exponents behavior points to the merging of the nFL state. The nFL state is strongly influenced by disorder of the system because of the non-isoelectronic mixture of the 3$d$ and 4$d$ bands. The band structure analysis assigns the evolution of ferromagnetism to the effects of the 5$f$-ligand hybridization. Our work also confirmed that the UCoGe compound represents a unique example of the system in the vicinity of the FM instability connected with evolution of the the nFL state. That nFL state can again develop in the neighboring doped systems. Further study of the region around the critical concentration including the measurements under the external pressure performed on single crystals is envisaged to deeply understand the background of the proposed nFL state.

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