CHIN. PHYS. LETT. Vol. 35, No. 6 (2018) 067102

Tuning the Heavy Fermion State of $CeFeGe_3$ by Ru Doping *

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(Received 26 March 2018)

We successfully synthesize a series of polycrystalline $CeRu_xFe_{1-x}Ge_3$ ($0 \leq x \leq 0.5$) samples, which are characterized using powder x-ray diffraction, resistivity and specific heat measurements. The expansion of the lattice constants with increasing x demonstrates the successful doping of Ru into the $CeFeGe_3$ lattice. Upon doping, it is found that the temperature up to which Landau–Fermi liquid behavior is observed in the resistivity is reduced. Meanwhile, there is also a pronounced increase in the resistivity coefficient and residual resistivity, as well as a clear upturn in C/T at low temperatures, suggesting that Ru doping may tune the system towards a quantum critical point.

PACS: 71.27.+a, 72.15.Qm, 75.40.−s DOI: 10.1088/0256-307X/35/6/067102

Heavy fermion systems have attracted much attention due to the rich variety of exotic ground states which can be realized.[1] The underlying physics is often described by the Doniach phase diagram, where the competition between the Ruderman–Kittel–Kasuya–Yosida (RKKY) and Kondo interactions gives rise to a magnetic ground state when the hybridization strength J between the conduction electrons and localized magnetic moments is small, or a paramagnetic Fermi liquid state with an enhanced effective mass (heavy fermion state) when J is sufficiently large.[1,2] Meanwhile, at the border between magnetic order and paramagnetism, there is often a non-Fermi liquid region in the vicinity of a quantum critical point (QCP). As a result of the relatively low energy scales, the ground state properties of heavy fermion systems are often readily tuned by parameters such as chemical doping, hydrostatic pressure and magnetic fields, and near a quantum critical point, novel phases such as unconventional superconductivity have been found.[3–8]

One particularly interesting family of heavy fermion compounds are the $CeTX_3$ (T = transition metal, and X = Si, Ge, Al) materials, which crystallize in the non-centrosymmetric tetragonal $BaNiSn_3$-type structure (space group $I4mm$). Many of them are heavy fermion compounds exhibiting magnetic order,[9–13] and in some cases such as $CeRhSi_3$ and $CeIrSi_3$, the antiferromagnetism is suppressed by applying pressure, leading to an unconventional superconducting phase in the vicinity of its disappearance.[14,15] On the other hand, some other materials with reduced lattice parameters, such as $CeRuSi_3$ and $CeCoSi_3$, are non-magnetic intermediate valence compounds, with significantly larger Kondo energy scales.[16,17] One curious example is that of $CeFeGe_3$, which is a nonmagnetic heavy fermion compound, but with a moderately large Kondo temperature of around 100 K and a Ce valence close to the integer value of 3.[18] Furthermore, the lattice volume is larger than the aforementioned intermediate valence compounds, being comparable with, or even larger than some of the antiferromagnetic $CeTX_3$ materials.[16,18] This suggests that $CeFeGe_3$ may be a good candidate for tuning towards a QCP from the non-magnetic side of the phase diagram. The possible existence of a QCP through chemical doping has been proposed in $CeCo_{1-x}Fe_xGe_3$.[19] However, here the substitution of Co for Fe actually corresponds to a slight compression of the lattice.

In this work, we synthesize a series of Ru-doped $CeFeGe_3$ polycrystalline samples, so as to tune the system towards a quantum critical point by introducing negative chemical pressure, reducing the Kondo hybridization strength. To characterize them, powder x-ray diffraction, resistivity and specific heat measurements have been performed.

Polycrystalline samples of $CeFe_{1-x}Ru_xGe_3$ ($0 \leq x \leq 0.6$, where x corresponds to the nominal Ru concentration) with mass of around 3 g were prepared by arc-melting stoichiometric amounts of the constituent elements under an argon atmosphere with purities of 99.99% for Ru and Ge, and 99.9% for Ce and Fe. The weight loss after melting was less than 1%, and the as-cast samples were annealed at 800℃ for one week. X-ray powder diffraction measurements were performed at room temperature using a PANalytical X'Pert MRD diffractometer with Cu $K_{\alpha 1}$ radiation. Measurements of the resistivity using the four-probe method and specific heat using the relaxation method were carried out on a Quantum Design physical prop-

*Supported by the National Natural Science Foundation of China under Grant Nos 11474251, 11604291 and U1632275, the National Key Research and Development Program of China under Grant Nos 2017YFA0303100 and 2016YFA0300202, and the Science Challenge Project of China under Grant No TZ2016004.

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erty measurement system (PPMS).

As shown in Fig. 1(a), the powder x-ray diffraction pattern of $CeFeGe_3$ matches well with previous results,[20] and the doped samples are consistent with the same structure, but with a systematic shift of the peak positions, as clearly shown in Fig. 1(b). The shift of the peaks to lower angles with increasing x is the consequence of an enlarged lattice spacing due to larger Ru atoms being partially substituted on the Fe sites. For the $x = 0.6$ sample, it can be seen that secondary phases are detected in the diffraction pattern, and moreover as shown in Fig. 1(b), the diffraction peaks corresponding to the main phase of the $x = 0.6$ sample are very close to those of the $x = 0.5$ sample. This suggests that for $x = 0.6$ there is no significant additional doping of Ru into the $CeFeGe_3$ lattice, and therefore in this work only the samples up to $x = 0.5$ are further characterized. The lattice constants and unit cell volume as a function of x are displayed in Figs. 1(c) and 1(d), respectively, where there is a nearly linear increase of the unit cell volume, reaching an overall increase of around 2% for 50% Ru doping. This expansion along all crystallographic directions indicates that the Ru dopant acts as a negative chemical pressure, which will reduce the hybridization strength between the $4f$ and conduction electrons.

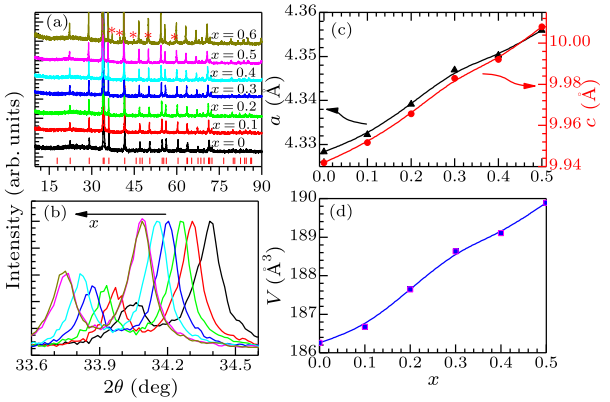

Fig. 1. (a) Powder x-ray diffraction patterns of polycrystalline samples of $CeFe_{1-x}Ru_xGe_3$ ($0 \leq x \leq 0.6$). The red vertical lines mark the positions of the peaks corresponding to $CeFeGe_3$, while the red asterisks mark the impurity peaks in the $x = 0.6$ sample. (b) Enlargement of the patterns near one of the major diffraction peaks, which systematically moves to lower angles with increasing x for $x \leq 0.5$. (c) The lattice constants a and c, and (d) the unit cell volume V plotted as a function of the Ru concentration x.

Figure 2(a) displays the temperature dependence of the resistivity of $CeFe_{1-x}Ru_xGe_3$ ($0 \leq x \leq 0.5$). For stoichiometric $CeFeGe_3$, there is a broad hump at around 100 K followed by Fermi liquid behavior at low temperatures, consistent with the previous report.[18] The substitution of Fe by Ru shifts the resistive hump to lower temperatures, which can be more clearly seen in Fig. 2(b), where the magnetic part of the resistivity (ρ_m) is presented after subtracting the resistivity of the non-magnetic analog $LaFeGe_3$. The maximum at T^* in $\rho_m(T)$ is usually attributed to the coherence associated with the Kondo scattering in the system. The inset of Fig. 2(b) plots T^* as a function of doping x, which suggests that the coherence temperature is lowered upon increasing the Ru concentration. This is in agreement with both the reduction of coherent scattering due to disorder, as well as an overall decrease of the Kondo energy scale with negative chemical pressure, as was expected from the Doniach phase diagram.[2]

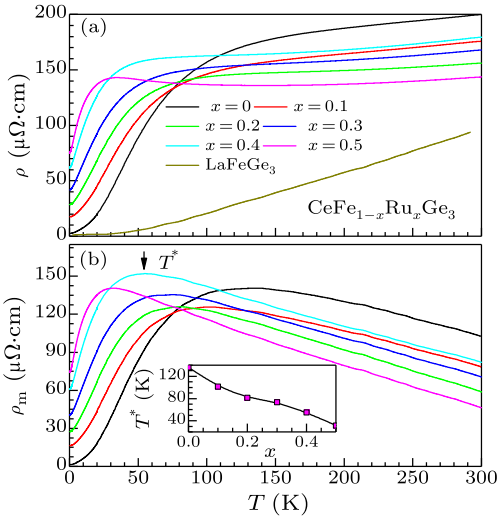

Fig. 2. (a) Temperature dependence of the electrical resistivity of $CeFe_{1-x}Ru_xGe_3$ ($0 \leq x \leq 0.5$). (b) The magnetic part of the resistivity ρ_m, after subtracting the data of the La-analog to remove the phonon contribution.[18] The temperatures at which the maximum of ρ_m occurs (T^*) are displayed are in the inset.

To track the Fermi liquid behavior, we fitted the resistivity data at low temperatures with $\rho = \rho_0 + AT^2$, which is displayed for four compositions in Fig. 3(a). With increasing the Ru concentration, the temperature region where T^2 behavior occurs becomes narrower. This is seen more clearly in Fig. 3(b), which displays the deviation of the resistivity from the fitted Fermi liquid behavior, showing that with increasing x, there is a decrease of the Fermi liquid temperature T_{FL} above which non-Fermi liquid behavior onsets. In addition, as more Ru atoms are doped into the lattice, the residual resistivity ρ_0 becomes larger. These trends suggest that as the lattice expands, the system moves away from the Fermi liquid behavior towards an extensive non-Fermi liquid region, which appears in many heavy fermion systems near a quantum critical point. Upon approaching such a quantum critical point, the stronger spin fluctuations may result in an enhanced residual resistivity, but it should also be noted that such an increase of the residual resistivity could be related to the greater disorder brought about by the increasing Ru doping.

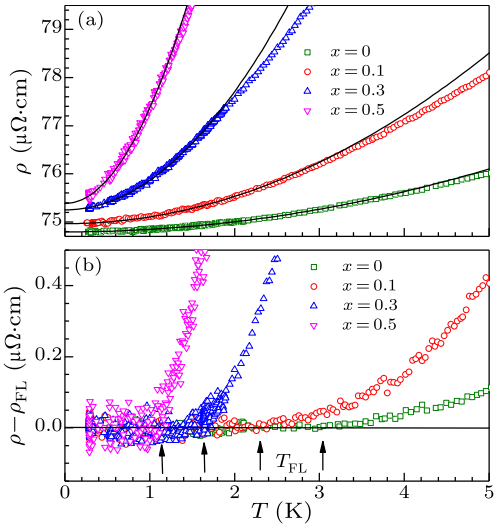

Fig. 3. (a) Low temperature resistivity for various doping concentrations. For clarity, the data of $x = 0$, 0.1 and 0.3 are shifted by 72, 57.5 and 34.6 μΩ·cm, respectively. The solid lines show the fits to the Fermi liquid dependence, i.e., $\rho_{FL} = \rho_0 + AT^2$. (b) Temperature dependence of the difference between the data and the fitted T^2 dependence, where T_{FL} corresponds to the temperature above which there is a deviation from Fermi liquid behavior.

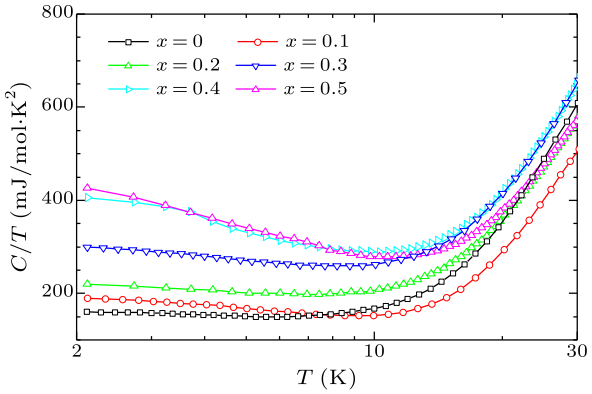

Fig. 4. Temperature dependence of the specific heat coefficient C/T of $CeFe_{1-x}Ru_xGe_3$ ($0 \le x \le 0.5$).

To further examine whether the system is tuned towards a quantum critical point by Ru doping, we measured the specific heat of the doped compounds, which are displayed in Fig. 4. For pure $CeFeGe_3$, the specific heat coefficient (C/T) at low temperatures reveals no magnetic transitions and an enhanced value of $\gamma = 160\,\mathrm{mJ/mol{\cdot}K^2}$, similar to previous reports.[18] With increasing the Ru content, the low temperature C/T values are enhanced, and for higher concentrations, the increase of C/T with decreasing temperature becomes more pronounced. For instance, at the doping concentration of $x = 0.5$, C/T does not saturate down to at least 2 K, reaching a value of around $420\,\mathrm{mJ/mol{\cdot}K^2}$. Such an increase is an indication of non-Fermi liquid behavior, and is consistent with the resistivity results, where the Fermi liquid temperature moves to lower temperature as the lattice expands.

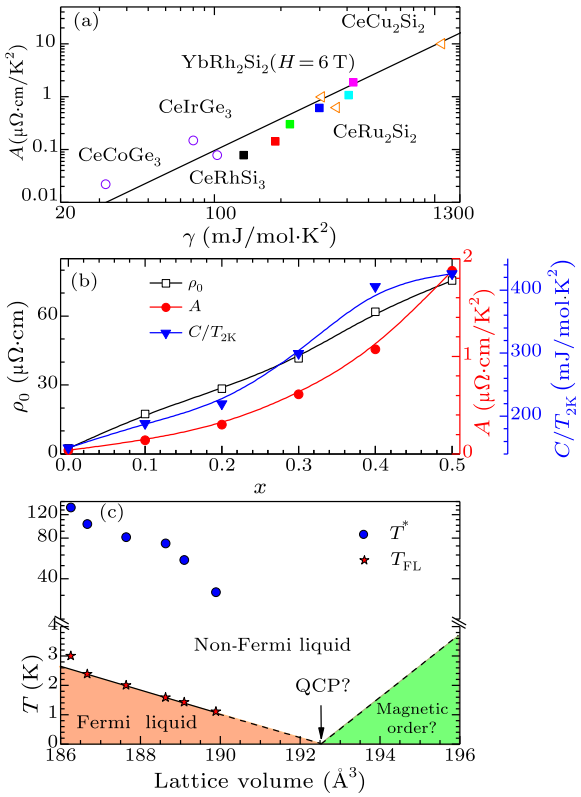

Fig. 5. (a) Resistivity coefficient A versus γ, where the purple circles correspond to other $CeTX_3$ compounds from Refs. [16,22], the orange triangles correspond to other heavy fermion materials from Refs. [21,23,24], and the square symbols are from this work. Different colors represent different doping concentrations. (b) Doping dependence of the A-coefficient and residual resistivity ρ_0 from fitting the resistivity with $\rho = \rho_0 + AT^2$, and the specific heat coefficient γ as C/T at 2 K. (c) Schematic phase diagram of this system, where T^* corresponds to the temperature of the maximum in the magnetic contribution to the resistivity, T_{FL} is the temperature below which the Fermi liquid behavior occurs, and the lattice volume is obtained from powder x-ray diffraction measurements. Increasing the Ru doping expands the lattice and suppresses the Fermi liquid temperature. Upon further doping, a quantum critical point would be expected to occur, along with the possible onset of magnetic order, as illustrated schematically by the dashed lines.

In Fig. 5(a), the A-coefficient versus γ is plotted on a logarithmic scale. For heavy fermion systems with a degeneracy N, the Kadowaki–Woods ratio A/γ^2 is given by[21]

$$\frac{A}{\gamma^2} \approx \frac{1 \times 10^{-5}}{\frac{1}{2}N(N-1)}\,\mu\Omega \cdot \mathrm{cm(mol \cdot K/mJ)^2}.$$

The behavior for the case of $N = 2$ is shown by the black line, and it can be seen that the results for all the $CeFe_{1-x}Ru_xGe_3$ compositions are very close to the expected value. Furthermore, experimental data taken for other heavy fermion compounds including some $CeTX_3$ materials are also displayed, which also fall close to this line.[16,21–24] These results suggest that the observed increase of A and γ can be understood as arising due to changes in the heavy fermion state, and therefore, their enhancement is likely due

to the system moving towards the quantum critical region. The findings from the resistivity and specific heat are summarized in Fig. 5(b), which displays ρ_0 and the A-coefficient from fitting the resistivity, and the specific heat coefficient γ (as C/T at 2 K), as a function of Ru-doping. All these quantities increase with the Ru content, consistent with our expectation that the system becomes heavier.

Figure 5(c) displays a schematic phase diagram for the $CeFe_{1-x}Ru_xGe_3$ system. Upon increasing the Ru concentration to expand the lattice volume, the Fermi liquid temperature is suppressed and an extended non-Fermi liquid region emerges, as expected from the Doniach phase diagram.[2] Consequently, further increase of the lattice volume, e.g., by partially substituting Fe with Os, may lead to a quantum critical point and the onset of magnetic order.

In summary, we have synthesized polycrystalline samples of $CeFe_{1-x}Ru_xGe_3$ and studied their physical properties to examine how the system is tuned upon expanding the lattice, to look for quantum criticality. The lattice constants of the doped samples increase systematically with x, indicating that this doping has a negative chemical pressure effect. The electrical resistivity data is consistent with a decrease of the coherence temperature and the Kondo energy scale upon doping. Moreover, the onset of Fermi liquid behavior is suppressed to lower temperatures, while there is a systematic increase of the specific heat coefficient, indicating that the system may be approaching a quantum critical point. Further doping studies and low temperature measurements are required to confirm the existence of a quantum critical point in this system, and to study the quantum criticality and any concomitant phases.

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