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# CeRuGe and CeRuSi: heavy fermion systems with some unusual features

**J.G. Sereni**[1], **N. Caroca-Canales**[2], **M. Kumar**[2], **N. Oeschler**[2], **M. Gomez Berisso**[1], **C. Geibel**[2]

[1] Low Temperature Div. CAB-CNEA, 8400 S.C. de Bariloche, Argentina
[2] Max Planck Institute for Chemical Physics of Solids, D-01187 Dresden, Germany

E-mail: `jsereni@cab.cnea.gov.ar`

**Abstract.**
We have investigated the physical properties of CeRuSi, its homologue CeRuGe and some doped La alloys. All of them present similar properties: large paramagnetic temperatures $\theta_P \approx$-100 K and the level off of $\chi(T)$ below $\approx$ 10 K in coincidence with the maximum decrease of $\rho(T)$, which starts to drop below 25 K. The respective $\gamma(CeRuSi) \simeq 0.18$ and $\gamma(CeRuGe) \simeq 0.15\,\mathrm{J/molK^2}$ coefficients reveal a heavy fermion character, with a Kondo temperature $T_K \approx 50$ K comparable to the crystal field splitting. In both compounds a broad maximum in $C_P(T)/T$ is observed around 5 K, whose origin is yet not clear. In contrast to the usual behavior observed in Kondo lattice systems, when Si is replaced by Ge $T_K \propto \theta_P$ and $1/\gamma$ practically does not decreases despite the unit cell volume of CeRuGe is about 3% larger than that of CeRuSi. We discuss possible origins for these unusual features.

Compounds with tetragonal CeFeSi structure [1] have attracted attention because of their interesting features like e.g. the quasi two dimensional properties. Recently, CeCoX (X=Si and Ge) [2] compounds were investigated concerning their capability for hydrogen absorption. Both compounds evidence a rather stable $Ce^{3+}$ state with weak Kondo interaction, c.f. $T_K < 20$ K and $\approx 6$ K respectively [3], but still well defined antiferromagnetic AFM ordering at $T_N = 8.8K$ and 4.8K respectively. Within that family of compounds, CeRuSi has only been the subject of marginal studies [4, 5] and therefore its physical properties are still poorly known. It was reported as a non-ordered heavy fermion like $CeRu_2Si_2$, whereas the low temperature properties of CeRuGe have not yet been reported. In order to gain a more precise knowledge on these compounds, we have started a thorough investigation of their physical properties by means of susceptibility $\chi$, resistivity $\rho$ and specific heat $C_P$ measurements. Samples of CeRuGe doped with La: $Ce_{1-x}La_xRuGe$, with $x = 0.2$ and 0.4, were also studied with the aim to produce a negative chemical pressure and drive Ce atoms closer to their $Ce^{3+}$ state.

Polycrystalline samples were prepared by arc-melting stoichiometric amounts of the components in an Argon atmosphere. Both CeRuSi and CeRuGe form in a very pronounced peritectic reaction, with the primary phase being $CeRu_2X_2$ (X = Si, Ge). As a result the as-cast samples contain a large amount of $CeRu_2X_2$ phase, which, according to our studies, needs a serious annealing process to be removed. We found that annealing for 2 weeks at or above 1100$^o$C, not far below partial melting of the sample, is necessary to get rid of the $CeRu_2X_2$ peaks in the XR-powder patterns. Nevertheless, even under these conditions a tiny amount ($< 1\%$) of this phase is still present, leading e.g. to a small ferromagnetic signal in $\chi(T)$ of

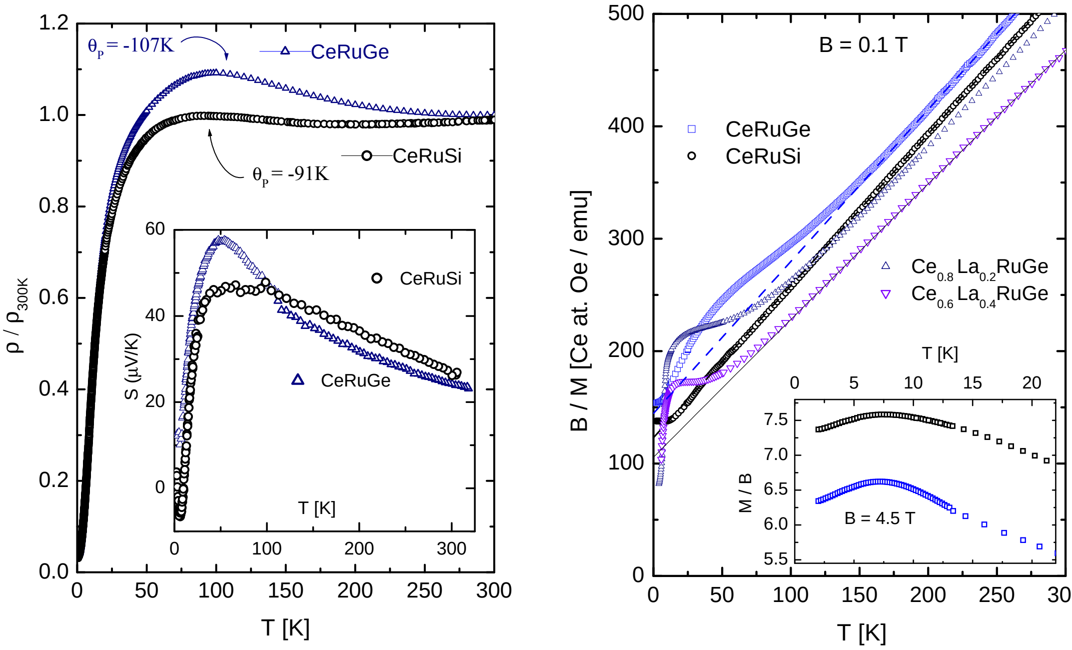

**Figure 1. Left:** Temperature dependence of electrical resistivity normalized at 300 K. Inset: thermoelectrical power as a function of temperature. **Right:** Temperature dependence of the inverse magnetic susceptibility. Straight lines indicate C-W law from which $\mu_{eff}$ and $\theta_P$ are extracted. Inset, magnetic susceptibility measurements in [$10^{-3}$ emu/Oe Ce at.] units, of both stoichiometric compounds at low temperature and high magnetic field.

CeRuGe originated from traces of $CeRu_2Ge_2$. However, samples annealed under slightly different conditions present the same main features as reported here, confirming that these properties are intrinsic to the CeRuX phase. The high quality of our CeRuX samples are e.g. demonstrated by a large residual resistivity ratio of RRR $\approx$ 30 for both compounds, see Fig.1-left.

Respective lattice parameters of the stoichiometric compounds are: $a = 4.2122 \AA$ and $c = 6.928 \AA$ for CeRuSi, and $a = 4.2869 \AA$ and $c = 6.889 \AA$ for CeRuGe. Despite of the unit cell volume and a-axis expansion of about 3% and 2% between Si and Ge compounds, the c-axis shrinks by 0.6%. This indicates a significant anisotropic structural expansion, reflected in a reduction of the 'c/a' ratio of about 2.3%, with expectable effects on the Ce-site symmetry.

High temperature $\rho(T)$ dependence of both compounds show their respective maxima $T^{\rho}_{max}$ at similar temperatures, see Fig. 1-left. There is, however, a difference in the electronic scattering intensity reflected in a larger maximum in CeRuGe. Such a difference occurs at the range of temperature where the first excited crystal field CF level is expected. Thermopower $S$ measurements also show respective maxima at slightly lower temperatures as the electrical resistivity, see inset in Fig. 1-left. The measured maximum value of $S(T)$ of CeRuSi is nearly 20% higher than the reported in the literature [4] and shows a pronounced minimum around 5 K after a sharp drop from quite high values. No low-T minimum was resolved for CeRuGe. The values for CeRuGe exceed those of CeRuSi and reach a maximum at 50 K with $S$=60$\mu$V/K.

Similar magnetic properties are observed in these compounds at high temperature ($T > 150$K)

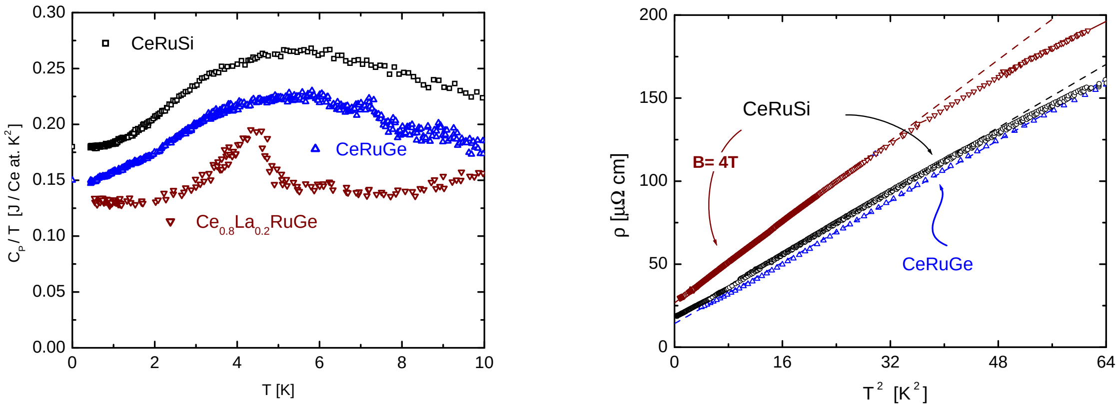

**Figure 2. Left:** Temperature dependence of specific heat in a $C_P vs T$ representation. **Right:** Low temperature resistivity variation vs. $T^2$, with zero and $B = 4$ T.

with an effective magnetic moment $\mu_{eff} = 2.43\mu_B$ extracted from the slope of the inverse of $\chi(T)$ depicted in Fig. 1-right. These values are slightly lower than the expected for the sixfold degenerated J=5/2 state: $\mu_{eff} = 2.54\mu_B$. The respective paramagnetic temperatures are $\theta_P = -91$ K (CeRuSi) and -107 K (CeRuGe). These values are compared in Fig. 1-left with $T^{\rho}_{max}$, both indicating a high value of their Kondo temperatures $T_K$. Nevertheless, below about $T \sim 120$K a clear difference between their $\chi(T)$ dependencies are observed. While CeRuSi follows a continuous Curie-Weiss C-W behavior down to about 20K, CeRuGe shows a remarkable departure below that temperature, which might be connected either with CF effects or with incipient valence fluctuation. Partial substitution of La for Ce lead to a shift of this feature to lower temperatures, which would be in favor of the latter explanation, but would then imply a strong decrease of the characteristic $4f$ energy with increasing La content. This feature is not supported by other properties like $\theta_P(x)$ which decreases only slightly from -107 K ($x$=0), -97 K ($x$=0.2) to -87 K ($x$=0.4), though the latter sample reaches a $\mu_{eff} \approx 2.54\mu_B$.

At low temperature, the magnetic susceptibility of both compounds flatten off below about 10 K, reaching a broad maximum centered around $T^{\chi}_{max}$= 8 K for CeRuSi and 7 K for CeRuGe, see the inset in Fig. 1-right. These maxima become well defined applying a field of 4.5T which saturates the contributions of spurious phases. Notably, $T^{\chi}_{max}$, better defined in CeRuSi, slightly decreases with magnetic field, c.f. from 8.8 K for B=2T to 7 K for B=4.5 T.

Specific heat of both compounds also show broad maxima centered at around 5.5 K in a $C_P(T)/T$ representation, see Fig. 1-left. At $T \to 0$, the respective Sommerfeld coefficients $\gamma(CeRuSi) \approx 0.18$ and $\gamma(CeRuGe)$=0.15 J/Ce at.K$^2$ confirm their heavy Fermion character. Both $C_P(T)/T$ initially increase as $\propto T^2$ before reaching their maxima with values about 50% above their respective $\gamma$ values. Respective Kondo temperatures, evaluated from specific heat as $T_K = \pi R/3\gamma$ [6] are in good agreement with those computed from $T_K = \theta_P/2 \approx 50$ K [7] for both compounds. This is also reflected in the small gain of entropy, which reaches only $\approx 1/4Rln2$ at 10 K, well below the value $\approx 1/2$ and $0.9Rln2$ observed at the same temperature in CeCoSi and CeCoGe, respectively [2, 3]. This confirms a much larger characteristic $4f$-energy in the Ru-based compounds than in the Co-based compound. Interestingly, preliminary data from sample $Ce_{0.8}La_{0.2}RuGe$ shows a $\gamma \approx$0.13 J/Ce at.K$^2$ value, which does not changes significantly from pure CeRuGe once normalized to Ce-atom. However, a small transition appears at $T_N$= 4.4K, as it can be seen in Fig. 2-left. Thus the increase of volume induced by this substitution does not lead to a significant decrease of $T_K$, as for the substitution of Ge for Si.

Taking profit that $\rho(T < 6K)$ increases $\propto T^2$, as depicted in Fig. 2-right, one can compare the $A'$ coefficient of $\rho = A'T^2$ with $\gamma$ following the Kadowaki-Woods K-W relation, $A/\gamma^2 = 1 \times 10^{-5}\mu\Omega\text{cm}(\text{K mol/mJ})^2$. The respective $A'$ coefficients 2.38 (CeRuSi) and $2.3\,\mu\Omega cmK^{-2}$ (CeRuGe) result in a $A'/\gamma^2$ ratio one order of magnitude larger than the expected K-W value. However, this is very likely due to an overestimation of the absolute $\rho(T)$ values. Our experimental values $\rho_{300} \approx 600\mu\Omega\text{cm}$ are at least a factor of five above the intrinsic value expected for this kind of metallic systems. Such large $\rho_{300}$ K values are quite commonly observed in Kondo lattices with some problems in the sample preparation process or inter-grain electrical contacts. Re-scaling the $\rho(T)$ values to more realistic ones brings the $A'/\gamma^2$ ratio closer to the K-W value. Interestingly, the range of temperature where the $\rho \propto T^2$ dependence is observed decreases with field, in agreement with the mentioned decrease of $T^{\chi}_{max}(B)$.

With $\chi_0$=$7.3 * 10^{-3}$ and $6.4 * 10^{-3}$ emu/mol for CeRuSi and CeRuGe respectively, and using $\mu_{eff}$= $2.54\mu_B$, one gets a Wilson ratio $Rw = \chi_0/\gamma_0(\pi k_B)^2/(\mu_0\mu_{eff}^2)$= 1.4 for both compounds, which is within the range expected for heavy fermion systems. Thus, this analysis confirms both compounds to be well behaved Fermi-Liquid systems at the lowest temperatures. This makes the initial increase of $C_P/T$, which for CeRuSi was already resolved in preliminary studies by Rebelsky et al. [5], even more intriguing. Since the maximum of $C_P(T)/T$ is located in the $T$ range where AFM order is observed in the Co-homologues, one might speculate than it is related to two-dimensional AFM-correlations. Because Ru being much larger than Co, it leads to a larger separation between (double) Ce-layers and, because of the stronger Kondo-interaction these correlations do not end into an AFM ground state as in CeCoSi or CeCoGe, but remains in a spin-liquid like state. In a purely localized Spin 1/2 square lattice systems one expects a maximum of $C_P(T)/T$ around $T$= 1/2 $J/k_B$, where $J$ is the exchange parameter between localized spins [8]. Therefore, this maximum deserves further investigations, especially with microscopic methods.

Comparing CeRuSi and CeRuGe physical properties, we conclude that Si by Ge substitution does not modify the $4f$ - conduction band interaction significantly since $T_K$ practically does not change despite of the unit cell volume increase. Only the a change of local symmetry seems to modify the electronic structure of the intermediate CF levels. Although both compounds behave as non-magnetic heavy Fermions, they present unusual maxima in $C_P$(T)/T and $\chi(T)$ at low temperature. Below those maxima, traces of magnetic interactions are observed whose nature is not yet understood. This requires to perform some microscopic measurements able to characterize local magnetic interactions.

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