The effect of chemical pressure on the ferromagnetic ordering of CeTX compounds

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Abstract. The transport and thermodynamic properties of CeTX (T = Au, Cu; X = Ge, Si) compounds have been studied. These well-ordered hexagonal compounds have shown ferromagnetic ordering anomalies in magnetic susceptibility, electrical resistivity and specific heat measurements at the ferromagnetic transition temperature $T_{\rm C}$, (10 K, 10 K and 15 K for CeAuGe, CeCuGe and CeCuSi, respectively). The location of magnetic ordering has been observed to be unstable under the influence of applied magnetic field, where the ferromagnetic ordering has been observed to shift upwards in temperature. However, the application of chemical pressure (dilution of Ce ions by non-magnetic isostructural La atoms) as observed from physical properties as well as magnetic properties measurements revealed a continuous tuning of $T_{\rm C}$ resulting in the ferromagnetic ordering temperature approaching 0 K as La content is increased. The calculation of the effective magnetic moment for small La content was observed to be 2.54 $\mu_{\rm B}$/mol of Ce, which is in agreement with the value of the full magnetic moment for Ce^{3+} ion. Powder x-ray diffraction (XRD) characterization of the dilution compounds indicated that the compounds retained their hexagonal crystal structure belonging to space group number 186 ($Ce_{1-x}La_x$)AuGe and 194 for ($Ce_{1-x}La_x$)CuGe and ($Ce_{1-x}La_x$)CuSi where the (0 0 0) Ce-site is partially substituted by La atoms. Rietveld refinement profile indicated that the lattice parameters a and c and the volume V of the dilution compounds increased with an increase in La content. This work presents the first results of the effect of isostructural substitution of Ce with La (($Ce_{1-x}La_x$)AuGe and ($Ce_{1-x}La_x$)CuGe. Measurements of magnetic susceptibility and specific heat for the dilution compounds gave the first evidence of tuning the ferromagnetic ordering temperature $T_{\rm C}$ to lower temperatures with the increase of La content in the compound.

1. Introduction

The study on quantum phase transitions (QPT) in local-moment systems has been mostly focussed on antiferromagnetic (AFM) systems. From the studies done on QPT, heavy fermion intermetallic compounds containing Ce, Yb, or U have been found to have unusual low temperature properties that appear to violate the dynamics of the Fermi-liquid (FL) metallic ground state paradigm [1]. These non Fermi liquid (NFL) materials exhibit weak power-law or logarithmic temperature dependences in various physical properties such as magnetic susceptibility, specific heat [2], and electrical resistivity at very low temperatures. NFL state then can be linked magnetic instability that arises at $T = 0$. Classical phase transition at nonzero temperatures, are driven by temperature as a control parameter with thermal fluctuations, a quantum phase transition is driven by a control parameter other than temperature, that is, external pressure, doping, or magnetic field at absolute zero, with quantum-mechanical

fluctuations. Such a control parameter tunes a system at the zero-temperature boundary from an ordered ground state towards a nonordered state crossing a quantum critical point [2].

The proximity of the suppressed magnetic phase transitions to the maximum T_C values, as well as more direct evidence of the instability of transition suggests the importance of magnetism, most likely, localized magnetism. A search into this phenomemon has been going on in condensed matter physics, particulary a search of quantum criticality in ferromagnetic compounds. It has been established from the previous studies that in compounds CeAuGe and CeCuGe, Ce carries a local moment with compounds ordering ferromagnetically at about 10 K, for CeAuGe [3] and CeCuGe [4], respectively. It is worth mentioning that these magnetic orders manifest anomalies in magnetic susceptibility, electrical resistivity and specific heat at T_C. In this work we present the first results of the effect of an isostructural substitution of Ce occupation site with La on the transition temperature T_C.

2. Experimental Procedure

Selected polycrystalline samples, $(Ce_{0.5}La_{0.5})AuGe$ and $(Ce_{0.7}La_{0.3})CuGe$ compounds were prepared by arc-melting stoichiometric quantities of the elements (purities in wt.%) Ce and La (4N), Cu (4N5), Ge and Si (6N) under-pressure in an ultra-high purity argon gas. The $(Ce_{0.7}La_{0.3})CuGe$ was subsequently annealed in an evacuated quartz tube at 800^0C for two weeks. This was followed by sample characterization through powder x-ray diffraction (XRD) and Rietveld refinement profile using General Structure Analysis Software (GSAS). The temperature dependent specific heat measurements of the compounds were performed using Physical Properties Measurement System (PPMS) from Quantum Design (QD) in San Diego. These measurements were performed in temperatures between 300 K and 1.9 K . Magnetic properties were measured using Magnetic Properties Measurement System (MPMS) in small applied magnetic field of 0.005 T ($(Ce_{0.5}La_{0.5})AuGe$) and 0.01 T for ($(Ce_{0.7}La_{0.3})CuGe$) between 395 K and 1.9 K.

3. Results

CeAuGe and CeCuGe are equiatomic intermetallic compounds confirmed to crystallize in a hexagonal crystal structure. The ordered ternary phase of CeAuGe crystallizes in the NdPtSb-type structure with the space group $P6_3/mc$ (number 186) (CeAuGe) and ZrBeSi-type structure with space group $P6_3/mmc$ (number 194) (CeCuGe). The unit cell is characterised by an elongated c-axis (almost double the length of the a-axis). The dilution compounds of the respective compounds were found to exhibit similar crystal structure and they remained as equiatomic compounds. As displayed in figure 1 the atomic arrangement of atoms in the unit cell show Ce atoms arranged in flat planes perpendicular to c-axis which are well separated by slightly puckered Au-Ge [3].

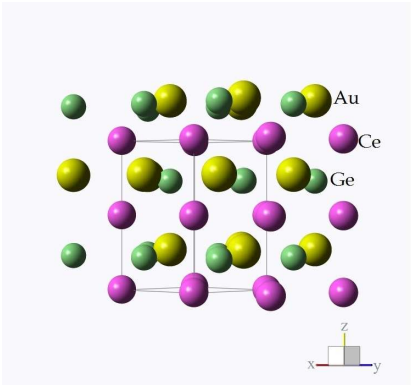

Figure 1. Crystal structure of CeAuGe, with slightly puckered -AuGe layer sandwiched between the Ce-layers.

Powder x-ray diffraction (XRD) recorded using Cu K_α radiation of wavelength $\lambda = 1.5406$Å confirmed the formation of single phase $(Ce_{0.5}La_{0.5})AuGe$ and $(Ce_{0.7}La_{0.3})CuGe$. The results of the Rietveld refinement are shown in figure 2. The refinable parameters in each compounds were instrument offset, the data background, unit cell parameters as well as full width half maximum (FWHM) of the peaks. It was observed that the lattice parameters (a, c) of these measured dilution compounds increased as the La element substituted some percentage of Ce-site. Table 1 lists the results output of Rietveld refinement profile of the CeAuGe, $(Ce_{0.5}La_{0.5})AuGe$, CeCuGe and $Ce_{0.7}La_{0.3}CuGe$ compounds. The observed lattice paramaters a, c and the volume V of the respective dilutions increase with the increase of La in the compound. More dilution compounds to complete the series of this study are in progress to conclusively determine the trend of the lattice parameters and the volume of the unit cell. This increase in the lattice parameters is ascribed to the change in the atomic dimensions of the rare earth site, as La partly replaces Ce.

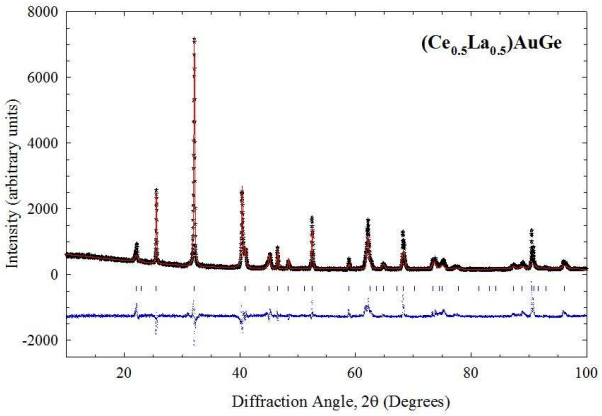

Figure 2. Experimental powder XRD data of $(Ce_{0.5}La_{0.5})AuGe$ (black symbols), Rietveld refinement fit (solid red line), difference curve (blue line) and the expected Bragg positions (pink vertical markers).

Table 1. The table of lattice parameters of $(Ce_{0.5}La_{0.5})AuGe$ and $Ce_{0.7}La_{0.3}CuGe$ as obtained from Rietveld Refinement fit.

	a(Å)	c(Å)	V(Å^3)
CeAuGe	4.4569(1)	7.9105(1)	136.078(1)
$(Ce_{0.5}La_{0.5})AuGe$	4.4598(1)	8.047(5)	136.611(2)
CeCuGe	4.299(5)	7.952(2)	127.252(3)
$(Ce_{0.7}La_{0.3})CuGe$	4.3175(5)	7.96(2)	128.5(5)

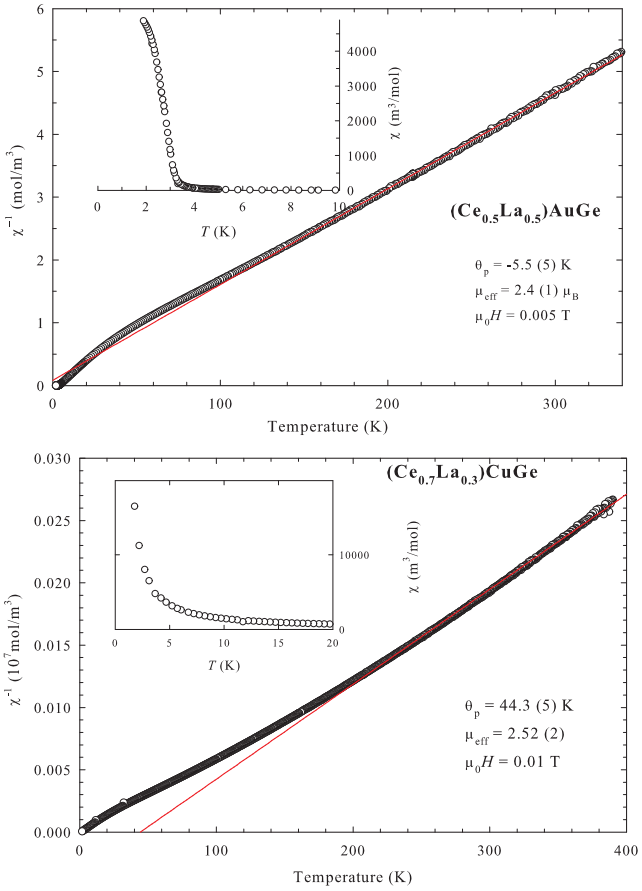

Figure 3. Temperature dependent inverse susceptibility of $(Ce_{0.5}La_{0.5})AuGe$ (top) and $(Ce_{0.7}La_{0.3})CuGe$ (bottom) where the insets show the low temperature data of magnetic susceptibility revealing long range ordering can be associated with ordering temperature.

Temperature dependent inverse susceptibility $\chi^{-1}(T)$ measured in the field-cooled (FC) mode in the temperature range between 350 K - 2 K (as there was no anomalous behaviour was expected above 350 K) and $\mu_0 H = 0.005$ T ($(Ce_{0.5}La_{0.5})AuGe$) and between 395 K - 2 K for $Ce_{0.7}La_{0.3}CuGe$ in constant applied magnetic field of 0.01 T is shown in figure 3. High temperature data ($T > 200$ K), is observed to follow the Curie-Weiss behaviour, and was fitted according to Curie-Weiss law:

$$\chi^{-1}(T) = \frac{3k_{\mathrm{B}}(T - \theta_{\mathrm{p}})}{N_A \mu_{\mathrm{eff}}^2}. \tag{1}$$

The fit yielded the paramagnetic Curie-Weiss temperature, θ_{p} = -5.5(1) K for $(Ce_{0.5}La_{0.5})AuGe$, which is an indication that the net interactions in the paramagnetic region of this compound are antiferromagnetic, despite the ferromagnetic ground state exhibited by this compound. An effective magnetic moment $\mu_{\mathrm{eff}} = 2.41(1)\ \mu_{\mathrm{B}}$ per Ce atom was calculated. This effective magnetic moment value is close to the theoretical value of $\mu_{\mathrm{eff}} = 2.54\ \mu_{\mathrm{B}}$. In the temperature region, $15\,\mathrm{K} \leq T \leq 160\,\mathrm{K}$ there is a deviation from Curie-Weiss behaviour. This deviation is attributed to the presence of crystal electric field effects (CEF) in this compound. In this regard, Ce in a hexagonal structure having a point symmetry of $\bar{3}$m, the ground state J-multiplet splits into

three doublets [5], which are mainly $|\pm M_J\rangle$ states where $|\pm M_J\rangle = \pm\frac{1}{2}$, $\pm\frac{3}{2}$ or $\pm\frac{5}{2}$ [6]. Within the framework of ionic model, the ground state of a configuration of Ce corresponds to $J = \frac{5}{2}$ ($L = 3, S = \frac{1}{2}$) and $g_J = \frac{6}{7}$. The insets on the top left corners of the figure 3, are the magnetic susceptibility data, exhibited to reveal the low temperature data. The long-range divergence is observed at about 3 K (from top inset), this could be associated with ferromagnetic ordering temperature T_C in this compound. From the inset in the bottom figure, the data diverges beyond our measuring temperature range, and this observation allows measurements to even lower temperatures (below 2 K). The fitted paramagnetic Curie-Weiss temperature, $\theta_p = 44.3(5)$ K for $(Ce_{0.7}La_{0.3})CuGe$ and the calculated effective magnetic moment $\mu_{eff} = 2.52(2)$ μ_B, were obtained, where μ_{eff} is in close agreement with the expected value for free Ce^{3+} ion [5] was obtained.

The specific heat data of the ternary CeAuGe has been confirmed to be at $T_C = 10$ K [3, 7] and that of CeCuGe was confirmed to be $T_C = 10$ K as well [4, 8]. The ordering temperatures are characterised by a λ-type anomaly in these data and are indicated by arrows in the inset of figure 4. The λ-type ordering temperature of the dilution compound $(Ce_{0.5}La_{0.5})AuGe$ is $T_C = 3$ K as taken from the maximum slope of the anomaly; whilst the ordering temperature of $(Ce_{0.7}La_{0.3})CuGe$ was observed at about $T_C = 5$ K. As the temperature increases beyond the ordering temperature, firstly there is an observable decrease in specific which is followed by a monotonous increase in the C_p data to maximum temperature, 300 K. This shift to lower temperatures as a result of chemical pressure which is achieved by the dilution of the Ce-moment, is contrary to the results obtained when the magnetic field is applied to equiatomic ternary compounds [4, 7, 9].

4. Conclusion

The isostructural substitution of Ce ions with La ions resulted in the shifting of lattice parameters as obtained from Rietveld refinement profile. The dilution compounds proved to retain similar structures as their ternary compounds. Magnetic susceptibility and specific heat measurements provided evidence of the tuning of ferromagnetic ordering towards lower temperatures. These results provide an opportunity to further investigate the possibility of NFL behaviour in these series of compounds.

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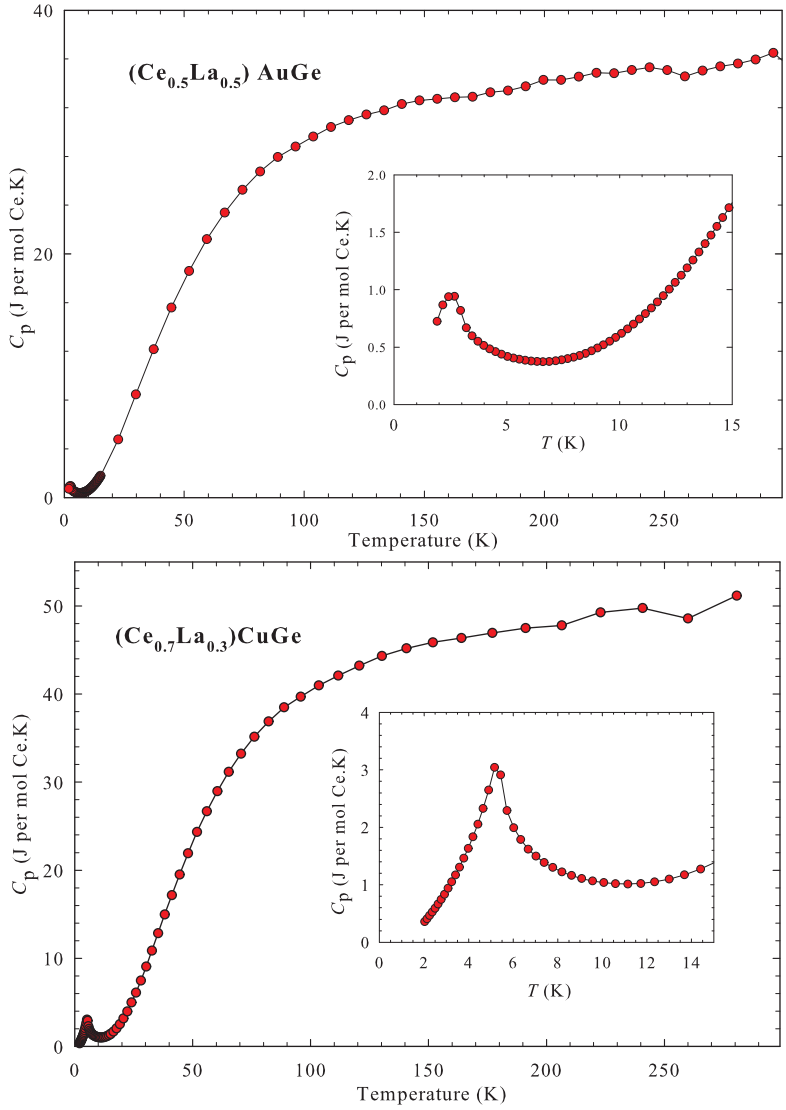

Figure 4. Specific heat of $(Ce_{0.5}La_{0.5})AuGe$ (top) and $(Ce_{0.7}La_{0.3})CuGe$ (bottom) where the insets show the low temperature data revealing a λ-type anomaly which can be associated with ordering temperature.