Remarkably Robust and Correlated Coherence and Antiferromagnetism in (Ce_{1-x}La_{x})Cu_{2}Ge_{2}
H. Hodovanets, S. L. Buďko, W. E. Straszheim, V. Taufour, E. D. Mun, H. Kim, R. Flint, and P. C. Canfield
Phys. Rev. Lett. 114, 236601 — Published 8 June 2015
DOI: 10.1103/PhysRevLett.114.236601
Remarkably robust and correlated coherence and antiferromagnetism in (Ce$_{1-x}$La$_x$)Cu$_2$Ge$_2$

H. Hodovanets$^{1,2}$, S. L. Bud’ko$^{1,2}$, W. E. Strasheim$^1$, V. Taufour$^{1,2}$, E. D. Mun$^2$, H. Kim$^2$, R. Flint$^{1,2}$, and P. C. Canfield$^{1,2}$

$^1$Ames Laboratory, Iowa State University, Ames, Iowa 50011, USA and
$^2$Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA

We present magnetic susceptibility, resistivity, specific heat, and thermoelectric power measurements on (Ce$_{1-x}$La$_x$)Cu$_2$Ge$_2$ single crystals (0 ≤ x ≤ 1). With La-substitution, the antiferromagnetic temperature $T_N$ is suppressed in an almost linear fashion and moves below 0.36 K, the base temperature of our measurements for x > 0.8. Surprisingly, in addition to robust antiferromagnetism, the system also shows low temperature coherent scattering below $T_{coh}$ up to ~ 0.9 of La, indicating a small percolation limit ~ 9% of Ce. $T_{coh}$ as a function of magnetic field was found to have different behavior for x < 0.9 and x > 0.9. Remarkably, $(T_{coh})^2$ at $H = 0$ was found to be linearly proportional to $T_N$. The jump in the magnetic specific heat $\delta C_m$ at $T_N$ as a function of $T_K/T_N$ for (Ce$_{1-x}$La$_x$)Cu$_2$Ge$_2$ follows the theoretical prediction based on the molecular field calculation for the $S = 1/2$ resonant level model.

PACS numbers: 71.10.Hf, 71.27.+a, 72.15.Qm, 75.20.Hr, 75.30.Kz, 75.30.Mb

Dilution studies of the Kondo lattice provide a unique probe to understand the interrelation between Kondo coherence and magnetic order. In a dilution study of the antiferromagnetically ordered Kondo lattice (Ce$_{1-x}$La$_x$)Cu$_2$Ge$_2$, we find a remarkably wide region of antiferromagnetic order and Kondo coherence up to $x = 0.8$ and $x = 0.9$, respectively, along with an unexpected scaling of $T_N \sim (T_{coh})^2$. This wide region appears to contradict current theoretical predictions for Kondo coherence alone, which state that coherence vanishes for much smaller $x$ [1], giving rise to either a broad region of non-Fermi liquid [2] or a Lifshitz transition [3, 4]. Our findings suggest that, in this system, magnetic correlations actually reinforce the Kondo coherence.

As a result of competition between Kondo effect and Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, Kondo lattices display a variety of ground states (long-range magnetic order, unconventional superconductivity, non-Fermi liquid, etc. [5–8]) and are characterized by multiple energy scales (antiferromagnetic $T_N$ or superconducting $T_c$ ordering temperature, the single-ion Kondo temperature $T_K$, the coherence temperature $T_{coh}$, and the crystal electric field (CEF) splitting). Ce-based compounds, both in coherent and diluted regimes, have been studied for more than four decades with the hope of understanding how coherence develops with increasing of Kondo impurity concentration (9–17 and references therein). For example, (Ce$_{1-x}$La$_x$)Pb$_3$ shows coherence up to $x = 0.15$ and single-ion Kondo scaling for a surprisingly wide range of $x$ and $T$ ($T_K$ is the same for these concentrations) [12, 18]. In the study of (Ce$_{1-x}$La$_x$)Ni$_2$Ge$_2$, the coherence was found up to $x = 0.4$ with impressive single-ion Kondo scaling in the coherent Fermi-liquid as well as diluted regimes [17].

Based on analysis of La dilution of CeCoIn$_5$ (for which $T_K$, $T_{coh}$, and CEF are well separated), a two-fluid description of the Kondo lattice was put forward [19]. It proposes two different energy scales for Kondo lattice: characteristic temperature $T^*$ ($T^* = T_{coh}$ for non-diluted, parent compound) that governs the intersite coupling of the f shells in the coherent Kondo lattice and the concentration-independent single-ion $T_K$, responsible for the on-site 4f- conduction-electron hybridization. $T_{coh}$ for this system was observed up to $x \sim 0.4$ [16].

In this work, we study La dilution of the Kondo lattice compound CeCu$_2$Ge$_2$ where $T_N \sim 4$ K [20–22] and the two excited CEF levels at $\Delta E_1 \sim 197$ K and $\Delta E_2 \sim 212$ K [23] are well separated from the ground state doublet. The measurements were performed on single crystals grown by the high temperature flux method [24–26]. The actual concentrations of La or Ce were assessed by wavelength dispersive x-ray spectroscopy (WDS) and the results of the Curie-Weiss fits of the temperature dependent susceptibility. The WDS values of La/Ce concentrations will be used throughout the text if not specified otherwise. La concentrations will be denoted by $x$ and Ce concentrations will be denoted by $y = 1 - x$ to avoid confusion. The details of samples growth, evaluation of La concentrations and measurement techniques can be found in the Supplementary Material [27].

An almost classic, mean-field-like second order AFM transition is clearly seen in the specific heat $C_p(T)$ data for CeCu$_2$Ge$_2$ (Fig. 1). As the amount of La is increased, the AFM transition moves to lower temperature and is still clearly observable for $x = 0.80$. When $T_N$ is suppressed enough, in addition to the AFM ordering, a broad maximum appears in the specific heat data starting from $x = 0.75$ (inset to Fig. 1), the position of which shifts slightly to lower temperatures as the La concentration is further increased. The maximum becomes almost indiscernible for $x = 0.99$. This maximum is associated with the Kondo temperature $T_K$ of a single-ion Kondo
impurity ($T_K > T_N$) [27].

A hallmark of the single-ion Kondo effect is the minimum and lower-temperature logarithmic dependence of the resistivity data. The zero-field, temperature dependent, in-plane, resistivity $\rho(T)$ data of (Ce$_{1-x}$La$_x$)Cu$_2$Ge$_2$ are shown on a semi-logarithmic plot in Fig. 2. For CeCu$_2$Ge$_2$, the $\rho(T)$ data exhibit a broad maximum at $\sim 100$ K associated with a thermal depopulation of the exited CEF levels as the temperature is decreased. At lower temperatures, the $\rho(T)$ plot shows a second broad maximum corresponding to a crossover from incoherent to coherent scattering of the electrons on the magnetic moments at $T_{coh} \sim 5.5$ K, characteristic of that of Kondo lattice compounds. The maximum is followed by (and actually truncated by) a kink corresponding to the AFM transition. As the amount of La is increased, the AFM transition moves to lower temperatures. The kink, corresponding to the AFM transition, becomes less discernible. Most intriguingly, the truncated maximum, at $T_{coh}$ for CeCu$_2$Ge$_2$, evolves into a broad maximum and remains present up to $x = 0.90$, Fig. 2(b). For $x = 0.92$, the resistivity data tend to saturation at the lowest temperature measured. This behavior in the resistivity is reminiscent of the single-ion Kondo impurity. For the three smallest Ce concentrations, the resistivity data display the minimum followed by a $-\log(T)$ dependence upon cooling to the lowest temperature. It is worth pointing out that the slightly temperature dependent minimum at $\sim 20$ K in the resistivity data is observed for all samples containing Ce. $T_{min}$ is proportional to the concentration of Ce, $y^{1/5}$, only for $0.01 \leq y \leq 0.08$ (see the Supplemental Material [27]) consistent with the single-ion Kondo impurity effect.

Thermoelectric power (TEP) can also provide information about the $T_{coh}$ and $T_K$ characteristic energy scales. Temperature-dependent thermoelectric power $S(T)$ data for (Ce$_{1-x}$La$_x$)Cu$_2$Ge$_2$ single crystals are shown in Fig. 3. The broad peak observed for LaCu$_2$Ge$_2$ at $\sim 75$ K ($\sim 0.2 \Theta_D$) is probably due to the phonon drag contribution expected at $0.1-0.3 \Theta_D$ [27, 37]. For all samples containing Ce, a broad, high-$T$ maximum due to (i) the thermal depopulation of the two excited CEF doublets [23] as the temperature is lowered and (ii) possibly phonon drag contribution is observed around 100 K. Since the energy separation between those two excited CEF levels is small, only one maximum at high temperatures is seen in the TEP measurements. The position of this maximum is almost unaffected by La substitution.

The TEP data of LaCu$_2$Ge$_2$ are positive over the whole temperature range measured. However, 0.01 of Ce is enough to change the functional dependence of the TEP below $\sim 24$ K: the TEP for $x = 0.99$ crosses zero twice by going through a low-$T$ minimum and has a low-$T$ maximum at $\sim 0.6$ K (see inset to Fig. 3). Such TEP behavior is expected for the Ce single-ion Kondo impurity [38–40]. For the highly La diluted samples, this low-temperature maximum is believed to correspond to the single-ion im-
purity Kondo temperature $T_K$. As the amount of Ce is increased, the absolute value of $S_{\text{min}}$ increases as well probably reflecting the amount of Ce ions and increased scattering associated with the increase of Ce.

The $T - x$ phase diagram for (Ce$_{1-x}$La$_x$)Cu$_2$Ge$_2$, Fig. 4, shows the characteristic temperatures and energy scales as a function of La concentration. $T_N$ (as determined from specific heat, magnetization, resistivity and TEP measurements) decreases almost linearly with $x$ and moves below the base temperature of 0.36 K or disappears for $x > 0.80$ and $T_{\text{coh}}$ extends down to $x = 0.90$. The low-temperature maxima in the TEP data seem to coincide with the $T_K$-values estimated from the specific heat data using a $T_{\text{max}} = 0.45 T_K$ criterion [41] rather well, here $T_{\text{max}}$ is the temperature where the maximum occurs. The $T_K$ values estimated using the Schotte and Schotte single-ion Kondo model fit [27, 42] of the specific heat data although lower, are still within the error bars of the ones estimated using the $T_{\text{max}} = 0.45 T_K$ criterion. The decrease of the Kondo temperature from ~ 4 K ($x = 0$) to ~ 1 K ($x = 0.99$) upon La substitution is consistent with the unit cell volume increase with $x$ in terms of Doniach phase diagram [43, 44] i.e. the system is tuned away from a quantum critical point (QCP). However, La-substitution dilutes out the magnetic moment of the system which is not accounted for in the Doniach phase diagram.

Based on the molecular field calculations for the $S = 1/2$ resonant level model, a close relationship between the specific heat jump, $\delta C_{\text{coh}}$, at the ordering temperature and the ratio between the two characteristic temperatures $T_K$ and $T_N$ for magnetic Ce and Yb Kondo systems with doublet ground states was found [45]. If the $T_K$-values shown in Fig. 4 are used and $T_K$ for CeCu$_2$Ge$_2$ assumed 4 K, (Ce$_{1-x}$La$_x$)Cu$_2$Ge$_2$ fits that description rather well, Fig. 5(a). This further supports the thought that the estimated $T_K$ values are reasonable and the CEF ground state is a doublet.

The presence of the AFM transition and linear dependence of it on $x$ to a high value of La is not unique to the (Ce$_{1-x}$La$_x$)Cu$_2$Ge$_2$ system. Such behavior of $T_N$ upon La-dilution was also observed in (Ce$_{1-x}$La$_x$)Pd$_2$Si$_2$ [13], as well as in (Ce$_{1-x}$La$_x$)Au$_2$Si$_2$, and (Ce$_{1-x}$La$_x$)Ag$_2$Si$_2$ [14]. The Ce-based parent compounds of these families, including CeCu$_2$Ge$_2$, order antiferromagnetically, with different ordering wave vectors, and belong to the same $I4/mmm$ space group of the tetragonal crystal structure. However, a progression of the $T_{\text{coh}}$, that corresponds to the crossover from incoherent to coherent scattering, with La substitution was not commented on for these systems, perhaps because $T_N$ and $T_{\text{coh}}$ could not be well separated. In this respect, (Ce$_{1-x}$La$_x$)Cu$_2$Ge$_2$ appears to be a unique system – the $T_{\text{coh}}$ is well separated from the AFM feature and extends all the way to ~ 0.9 of La.

Remarkably, $(T_{\text{coh}})^2$ is linearly proportional to $T_N$, Fig. 5(b), over wide range of $x$ and both seem to go to zero at $x \sim 0.9$. As of yet, there is no theory to explain a clear and compelling dependence of $T_{\text{coh}}$ on $T_N$.

In addition, a different field-dependence of the $T_{\text{coh}}$-value was found in the single-ion regime, Fig. 5(c), which also supports the conclusion that $y \leq 0.09$ defines the limit of the single ion regime in the zero-field limit (Fig. 5(c) is based on the data given in the Supplementary Material [27]). The functional dependence of $T_{\text{coh}}$ on $H$ for $x = 0.92$ is clearly different from that for smaller La concentrations, i.e., for $x < 0.9$, $T_{\text{coh}}$ saturates to a
finite value as $H \to 0$, and this is not the case for the $x = 0.92$ data. Also, for $x = 0.92$, there is no $T_{coh}$ at $H = 0$ and $T_{coh}$ is induced by magnetic field for all applied fields as opposed to smaller La concentrations.

This dilution study raises a number of questions/challenges for theories of the Kondo lattice. In particular, why do $T_N$ and $T_{coh}$ persist out to 90% La substitution? And why does $T_N$ scale as $(T_{coh})^2$? In a simple percolation picture, this persistence indicates that the Kondo lattice has a low percolation threshold, consistent with a three-dimensional network with further neighbors; e.g. - the cubic lattice with second and third neighbor interactions has a percolation threshold of 0.0976 [46, 47]. Once coherence is established, the system can develop an AFM transition. At a more qualitative level, given that the clear AFM ordering signatures persist out to $x = 0.8$, indicating that there is clear coupling and interaction between the remains of the Ce-sublattice, it is not at all surprising that this same coupling and interactions support coherence between ions.

More sophisticated numerical studies of the dilute Kondo lattice give a crossover between coherent and single-ion Kondo behaviors at $x \approx 0.1$ only for very low conduction electron carrier densities, $n_c \ll 1$ [2, 4]. There are no experimental indications that $n_c$ for CeCu$_2$Ge$_2$ is so small, and this is contraindicated by the observation that $T_{coh} > T_K$ [48] and by bandstructure calculations [49]. The large discrepancy between these numerical studies and our results suggests that large intersite correlations are essential to Kondo coherence in the dilute limit of (Ce$_{1-x}$La$_x$)Cu$_2$Ge$_2$, unlike in other materials such as (Ce$_{1-x}$La$_x$)CoIn$_5$ [16, 19] and (Ce$_{1-x}$La$_x$)Pb$_3$ [12, 18]. The unusual scaling of $T_N$ with $(T_{coh})^2$ is unexpected and counters results of the two-fluid model, where $T^*$ and $T_N$ are expected to behave similarly [19].

In summary, La substitution drives $T_N$ in a roughly linear fashion from $\sim 4$ K (for $x = 0$ ) to below 0.36 K, the base temperature of our measurements, for $x > 0.8$. However, $T_{coh}$, corresponding to the crossover from incoherent to coherent scattering, was observed up to $x \sim 0.9$. This indicates that the percolation limit of the lattice of Ce ions is rather small and implies the 3D nature of the Kondo “clouds”. Non-non-Fermi liquid or Fermi liquid behavior that would indicate a quantum critical point (QCP) was observed in the thermodynamic and transport measurements upon suppression of $T_N$. We find $y \leq 0.09$ is the single ion regime with $T_{coh}$ showing different behavior as a function of $H$ for $x > 0.9$ and $x < 0.9$. Remarkably, $(T_{coh})^2$ at $H = 0$ was found to be linearly proportional to $T_N$ over wide range of $x$. (Ce$_{1-x}$La$_x$)Cu$_2$Ge$_2$ appears to be the only system where $T_{coh}$ is observed down to $x = 0.9$ of La, $T_{coh}$ is well separated from magnetic ordering and single impurity effects, and $T_{coh}$ shows a parabolic dependence on $T_N$. Our results indicate that (Ce$_{1-x}$La$_x$)Cu$_2$Ge$_2$ is particularly compelling system and may be very useful for understanding the Kondo and RKKY effects.

**Acknowledgment** The authors would like to thank J. Schmalian, P. Riseborough, Z. Fisk, B. C. Sales, J. D. Thompson and F. Steglich for insightful discussions. This work was done at Ames Laboratory, US DOE, under contract #DE-AC02-07CH11358. This work was supported by the US Department of Energy, Office of Basic Energy Science, Division of Materials Sciences and Engineering. E.D. M and H. K. were supported by the AFOSR-MURI grant No. FA9550-09-1-0603.
