The γ → α isostuctural transition in the Ce₀.9₋ₓLaₓTh₀.₁ system is measured as a function of La alloying using specific heat, magnetic susceptibility, resistivity, thermal expansivity/striction measurements. A line of discontinuous transitions, as indicated by the change in volume, decreases exponentially from 118 K to close to zero with increasing La doping and the transition changes from being first-order to continuous at a critical concentration 0.10 ≤ x ≤ 0.14. At the tricritical point, the coefficient of the linear T term in the specific heat γ and the magnetic susceptibility start to increase rapidly near x = 0.14 and gradually approaches large values at x=0.35 signifying that a heavy Fermi-liquid state evolves at large doping. Near x_c, the Wilson ratio, R_W, has a value of 3.0, signifying the presence of magnetic fluctuations. Also, the low-temperature resistivity shows that the character of the low-temperature Fermi-liquid is changing.

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Bridgman’s discovery of the first-order volume collapse between the γ- and α-phases of cerium in the 1930’s has proven one of the most fundamental problems in critical phenomena [1, 2]. Subsequent studies carried out at room temperature showed that the transition between the high-temperature γ-phase and the low-temperature α-phase is isostuctural (fcc-to-fcc) and is manifested by a large decrease in volume (as much as 17%) at a pressure 0.7 GPa [3, 4]. The magnetic susceptibility and specific heat of the γ-phase are quite large and similar to those expected of a system with local moments, while in the α-phase the susceptibility is Pauli-paramagnetic and the coefficient of the linear T term in the specific heat is unusually small (12.8 mJ K⁻²mol⁻¹) for a compound with non-localized 4f electrons [5].

The puzzling properties of γ → α phase transition in elemental cerium has lent itself to many theoretical models based on often contradictory interpretations of the experimental data. First, L. Pauling [6] and W. H. Zachariasen [7] independently suggested that in the phase transition the f electrons responsible for the magnetic properties are squeezed into the valence band. In this picture, the volume collapse occurred as a result of the increased bonding by the valence electrons. This was thought to occur since the wavefunctions of the bonding electrons have smaller radii. The Pauling-Zachariasen promotional model was challenged when Gustafson et al. [8, 9] performed positron lifetime and angular correlation measurements of the annihilating photons in γ- and α-Ce that indicated that there was no significant change in the number of f electrons. These observations were supported by Compton scattering data [10], as well as x-ray absorption measurements of the L edges [11], which also showed no substantial valence fluctuation at the transition. In view of the experimental evidence, Johansson [12] concluded that the promotional model was incorrect and suggested that the γ → α phase transition was a Mott transition in which the localized magnetic 4f electron states were transformed into a broad non-magnetic 4f band of Bloch states. However, photoemission experiments [13, 14] showed that in both phases the f level was primarily located at an energy between 2 and 3 eV below the Fermi energy, contradictory to what Johansson envisaged where, in the itinerant state, the 4f band should cut across the Fermi energy. Recently, this conclusion has been reinforced by magnetic form factor [15] and phonon densities of states [16] measurements that showed that the magnetic moments remain localized in both phases.

On the basis of photoemission measurements, Allen and Martin suggested that the phase transition was due to a Kondo volume collapse [17]. Here, the 4f level is always below the Fermi energy and results in a localized 4f magnetic moment. The transition is due to the competition between the entropy of the six-fold degenerate magnetic ion in the high-temperature state and the binding energy of a Kondo singlet (∼ k_BT_K) formed in the low-temperature state by binding a conduction electron to the local moment. One of the signatures of the Kondo model is that the Wilson ratio, i.e. the dimensionless ratio of the susceptibility to the specific heat, R_W

\[ R_W = \frac{4\pi^2k_B^2}{3(\mu_B)^2}\frac{\chi(0)}{\gamma}, \]  

should have a value intermediate between 2, for a spin one-half model, and unity, as expected either in the limit of large spin degeneracy (2j + 1) ≫ 1 or for non-interacting electrons.
concentrations the transition is purely continuous. After the transition, the two critical points coalesce, and for higher concentrations, the transition temperature decreases exponentially, and the hysteresis goes to zero (within experimental error) at $0.10 \leq x_c \leq 0.14$, signifying a tricritical point. (b) The variation in the electronic specific heat $\gamma$ is shown along the left $y$-axis, whereas the thermal hysteresis $\gamma$ is shown on the right $y$-axis. Near $x_c$ one sees a peak in $R_W$, signifying the onset of a heavy Fermi-liquid state.

Although in elemental Ce, the vibrational entropy change per atom is estimated to account for about half the total entropy change [18], the entropy change due to phonon softening at the transition of doped materials is small [19]. Therefore, the entropy of the low-temperature phase must play an important role in driving the transition. Recently, Dzero et al. have suggested that, if the low-temperature phase is non-magnetic and the high-temperature phase has local moments, then application of an magnetic field, $B$, should result in a depression of the critical temperature [20]. Dzero et al. predicted that the phase-boundary in the $(B,T)$-plane should have a semi-elliptical form. Since doping with Th was known to suppress an unwanted portion of the $\beta$-phase and also reduce the transition temperature, it was possible to find a doping level at which the phase boundary could be measured in the accessible field ranges. The observed phase boundary [21] was found to be consistent with the predictions of Dzero et al. [20], albeit with small modifications due to the cubic crystal field splitting. For a range of higher doping concentrations, it was shown that there was a first-order transition line segment with a critical point at each end [21, 22, 23]. At a critical concentration, the two critical points coalesce, and for higher concentrations the transition is purely continuous.

In this paper we show that, with an optimal level of doping, it is possible to push the transition temperature close to 0 K, so that the $\gamma \rightarrow \alpha$ phase transition occurs as a tricritical point. Furthermore, as the critical concentration is approached, under ambient pressure, the coefficient $\gamma$ of the linear $T$ term in the heat capacity shows a rapid increase, and is still increasing on the La-rich side of the transition. The magnetic susceptibility follows the same trend as the concentration is varied. This suggests that the transition occurs from a state characterized by pudgy electronic masses to a heavy fermion state. However, the Wilson ratio peaks at a value above 2 for a narrow range of concentrations where the specific heat and susceptibility vary most rapidly with the doping concentration. That is, there is an increase in the Wilson ratio at the critical concentration as determined from the volume change.

Samples are prepared by arc melting the 99.99 % metals in an atmosphere of Ar. The ingot is melted several times on each side and then sealed in quartz and annealed for 5 days at 480 C. Chemical composition of the ingots were made by inductively coupled mass spectrometry. Specific heat, magnetic susceptibility, and thermal expansivity were measured on a Quantum Design Physical Properties Measurement System (PPMS). Specific heat was measured by a thermal relaxation technique. Given the large volume change on cooling it was necessary to fabricate a spring-loaded copper screw in a copper sample holder. The holder was attached to the platform with a thin layer of Apiezon N grease. The specific heat of the copper sample holder and the specific heat of Apiezon N were measured separately and subtracted from the total specific heat to obtain the specific heat of the sample. Measurements were performed below 20 K. The magnetic susceptibility was measured in a vibrating sample mag-

![FIG. 1](image1.png)

**FIG. 1:** (a) The effect of alloying on the $\gamma \rightarrow \alpha$ transition is shown along the left $y$-axis, whereas the thermal hysteresis is shown on the right $y$-axis. The transition temperature decreases exponentially, and the hysteresis goes to zero (within experimental error) at $0.10 \leq x_c \leq 0.14$, signifying a tricritical point. (b) The variation in the electronic specific heat $\gamma$ is shown along the left $y$-axis, whereas the thermal hysteresis $\gamma$ is shown on the right $y$-axis. Near $x_c$ one sees a peak in $R_W$, signifying the onset of a heavy Fermi-liquid state.

![FIG. 2](image2.png)

**FIG. 2:** Temperature variation of the resistivity for concentrations above and below $x_c$. For convenience, the resistivity is scaled with respect to the resistivity measured at $T=2K$, $R_{2K}$, which has the values of $3.4 \times 10^{-4} \Omega cm$ and $9.14 \times 10^{-5} \Omega cm$ for $x=0.25$ and $x=0.05$, respectively. The inset shows $R(t)/R_{2K}$ for $x=0.14$, near $x_c$. 
FIG. 3: The magnetic susceptibility as a function of temperature is shown for La concentrations below and above $x_c$. We note the discontinuous nature of the transition for $x = 0.05$, whereas the transition features a continuous cusp at $x = 0.20$. Also, we note the thermal hysteresis phenomenon present below $x_c$, disappears above $x_c$. In order the emphasize the $\alpha$ phase, the transition from Curie-Weiss behavior (high-temperature $\gamma$ phase) into a Pauli temperature-independent susceptibility is shown on a logarithmic scale in the inset. The inset also shows the susceptibility for a third composition near $x_c$.

netometer (VSM) in fields up to 9 T with a frequency of 40 Hz. The coefficient of linear thermal expansion $\alpha$ was measured in a three-terminal capacitive dilatometer (see Ref. [24] for details of the apparatus).

Figure 4(a) shows the suppression of the transition temperature (as measured in the thermal expansion) and the thermal hysteresis (as measured in the magnetic susceptibility) as a function of La doping. One sees a crossover from a line of discontinuous transitions, where the hysteresis is 5 K at $x \lesssim 0.14$ to a line of continuous transitions at $x \geq 0.14$. This result is mirrored in the electronic specific heat and Wilson ratio as shown in Fig. 4(b). Here, a low-temperature heavy Fermi-liquid state develops for concentrations greater than $x_c$, where the transition temperature of the continuous $\gamma \rightarrow \alpha$ is close to zero. The Wilson ratio indicates that the heavy Fermi-liquid state does not evolve directly from the $\alpha$ Fermi-liquid phase, as it shows significant deviations from the value of 2 for a small range of concentrations around the critical concentration. This finding is supported by the low-temperature variation of the resistivity which shows a $T^2$-like dependence for concentrations above and below $x_c$, as is expected for a Fermi liquid (see Fig. 2). The Kadowaki-Woods $x \leq x_c$ is in agreement with the expected value, but a good $T^2$ fit could not be obtained for $x \geq x_c$. However, for concentrations near $x_c$ the resistivity varies linearly with $T$ down to 1.9 K which was the lowest temperature measured. This type of change in the temperature variation of the resistivity is frequently found near quantum critical points, which is what is expected when a critical point is moved to zero.

The magnetic susceptibility data for compositions spanning $x_c$ are shown in Fig. 3. These data were recorded at a magnetic field of $H = 9$ T with a cooling/warming rate of 0.2 K/min. For the $x = 0.05$ sample one sees a discontinuous change (at 115 K on cooling) from Curie-Weiss behavior in the $\gamma$-phase to a temperature-independent susceptibility below the transition. Conversely, for $x = 0.20$ one sees a continuous change with negligible thermal hysteresis $\Delta T$ ($\Delta T \lesssim 0.5$ K). In the $\alpha$-Ce phase of this sample, the susceptibility does not return to a temperature-independent susceptibility which we take as a sign of sluggish kinetics. We have observed sluggish kinetics in the thermal expansion and in previous transport measurements in magnetic fields [21]. In the Fig. 3 inset, the susceptibility is shown on a log-T scale to emphasize the low-temperature phase. Here a third composition is added to show the evolution from a first-order to a continuous transition.

The phase boundary in the heavy Fermi-liquid phase was fit using the Fermi-liquid model [22, 23], whereas in the paramagnetic phase we used the two-level model proposed by Aptekar' and Ponyatovskiy (A-P) [24, 26] for the isomorphous $\gamma \rightarrow \alpha$ transformation in cerium metal.

FIG. 4: The $\gamma \rightarrow \alpha$ transition as measured by the thermal expansivity is shown as a function of $x$ in the main figure. Mirroring the susceptibility behavior, the discontinuous nature is apparent at compositions below $x_c$. At compositions above $x_c$, the volume expansivity, $\beta$, is fit to the A-P model. Inset (a) shows also shows the evolution of the critical point in $\Delta V/V$, while the magnetic field dependence is shown in inset (b).
The crucial input to the Fermi-liquid model is the volume dependence of the Fermi-liquid temperature. On defining the Fermi-liquid temperature as being proportional to $\gamma^{-1}$, we find that in the Fermi-liquid model the transition is driven by an abrupt change in $\gamma^{-1}$ that occurs over a small range of molar volumes. The cause for an abrupt variation of the Fermi-liquid temperature might be considered outside the scope of the Fermi-liquid model, but might be due to the existence of a critical interatomic spacing for Ce $^{[27]}$. Whereas the Fermi-liquid model describes the condensation of electrons into a homogeneous state at low temperatures, the A-P model is a thermodynamic model based on the notion of the equilibrium in an inhomogeneous binary phase. Because the phase boundary is determined by the free energy, it is possible in principle to determine the energy difference between the two phases, $\Delta E$, entropy difference $\Delta S$, volume difference $\Delta V$ and energy of mixing $U$, from knowledge of the temperature dependence of the boundary. A practical procedure is to integrate the experimental boundary between 10 and 300K to get $\Delta V$, and find the remaining three parameters from the data using the Levenberg-Marquardt optimization. A fit of the A-P model to the measured thermal expansion is shown in Fig. 4. In this figure the volume expansivity, $\beta/\gamma$ versus $T$ is plotted to show the suppression of the discontinuous $\gamma \rightarrow \alpha$ transitions. At La compositions $x \leq x_c$ one sees the first-order character of the transition. Here the transitions are too sharp to be fit by the A-P model. For $x \geq x_c$, one sees a continuous transition. The evolution from first order to continuous is mirrored in the volume shown in the inset (a) of Fig. 4. Here one clearly sees the critical point at $x = 0.14$ shown by the gentle cusp near 20 K. At this composition magnetic fields move the phase boundary of the transition in $H^2 T^2$ space as can be inferred from inset (b). Combining results from $^{[21]}$ and the current thermodynamic data, one finds the phase $T-H-x$ diagram shown in Fig. 5a. Similarly, combining pressure results from $^{[22]}$ one finds a phase $T-p-x$ diagram shown in Fig. 5b. In each case the surface marks the phase boundary between the high-temperature local-moment phase and the low-temperature Fermi-liquid phase. The tricritical line indicates a change in the transition from first to second order. The tricritical line occurs at concentrations where the character of the low-temperature Fermi-liquid is rapidly changing, and the resistivity shows changes characteristic to a system in the vicinity of a quantum critical point.

In conclusion, in this paper we have shown that it is possible to move the transition temperature close to 0 K, so that the $\gamma \rightarrow \alpha$ phase transition occurs as a tricritical point. At ambient pressure, the coefficient $\gamma$ of the linear $T$ term in the heat capacity and the magnetic susceptibility show a rapid increase as the critical concentration is approached. This increase continues on the La-rich side of the transition. Based on these observations, we suggest the transition occurs between a state characterized by pudgy electronic masses and a heavy fermion state. The Wilson ratio reaches a value above 2 for a narrow range of concentrations near $x_c$, signifying the presence of magnetic fluctuations. Here the character of the low-temperature Fermi-liquid is rapidly changing, and the resistivity shows changes characteristic to a system in the vicinity of a quantum critical point.

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