Tricritical Phenomena at the $\gamma \rightarrow \alpha$ Transition in $Ce_{0.9-x}La_xTh_{0.1}$ Alloys

J. C. Lashley,[1] A. C. Lawson,[1] J. C. Cooley,[1] B. Mihaila,[1] C. P. Opeil,[1] L. Pham,[1] W. L. Hults,[1] J. L. Smith,[1]
G. M. Schmiedeshoff,[2] F. R. Drymiotis,[3] G. Chapline,[4] S. Basu,[5] and P. S. Riseborough[5]
[1]*Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*
[2]*Department of Physics, Occidental College, Los Angeles, California 90041, USA*
[3]*Department of Physics, Clemson University, Clemson, South Carolina 29634, USA*
[4]*Lawrence Livermore National Laboratory, Livermore, California 94551, USA*
[5]*Physics Department, Temple University, Philadelphia, Pennsylvania 19122, USA*
(Received 17 March 2006; published 5 December 2006)

The $\gamma \rightarrow \alpha$ isostructural transition in the $Ce_{0.9-x}La_xTh_{0.1}$ system is measured as a function of La alloying using specific heat, magnetic susceptibility, resistivity, thermal expansivity or striction measurements. A line of discontinuous transitions, as indicated by the change in volume, decreases exponentially from 118 K to close to 0 K with increasing La doping, and the transition changes from being first-order to continuous at a critical concentration, $x_c \approx 0.14$. At the tricritical point, the coefficient of the linear T term in the specific heat γ and the magnetic susceptibility increase rapidly near x_c and approach large values at $x = 0.35$ signifying that a heavy Fermi-liquid state evolves at large doping. The Wilson ratio reaches a value above 2 for a narrow range of concentrations near x_c, where the specific heat and susceptibility vary most rapidly with the doping concentration.

DOI: 10.1103/PhysRevLett.97.235701　PACS numbers: 64.60.Kw, 05.70.Fh, 05.70.Jk, 75.30.Mb

Bridgman's discovery of the 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 isostructural (fcc-to-fcc) and is manifested by a large decrease in volume (as much as 17%) at a pressure of 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 typical ($12.8\ \mathrm{mJ\,K^{-2}\,mol^{-1}}$) for a compound with nonlocalized $4f$ electrons [5].

The puzzling properties of the $\gamma \rightarrow \alpha$ phase transition in elemental Ce have lent themselves 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 wave functions 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 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 $\gamma \rightarrow \alpha$ phase transition was a Mott transition in which the localized magnetic $4f$ electron states were transformed into a broad nonmagnetic $4f$ 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 ($\sim k_B T_K$) formed in the low-temperature state by binding a conduction electron to the local moment. The Wilson ratio, i.e., the dimensionless ratio of the susceptibility to the specific heat, R_W, 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 $(2j + 1) \gg 1$ or for noninteracting electrons.

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 local moments of the high-temperature phase must play an important role in driving the transition. Recently, Dzero *et al.* have suggested that, if the low-temperature phase is nonmagnetic and the high-temperature phase has local moments, then application of a 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. Because doping with Th was known to suppress an unwanted portion of the β-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 [21–23]. At a critical concentration, the two critical points coalesce, and for higher concentrations, the transition is continuous. Eliashberg and Capellmann [24], and more recently Dzero *et al.* [25], have predicted that f-electron fluctuations lead to termination of the first-order phase line in the Ce system.

In this Letter, we show that, with an optimal level of doping, it is possible to push the transition temperature close to 0 K, so that the $\gamma \longrightarrow \alpha$ phase transition occurs as a tricritical point. Furthermore, as the critical concentration is approached under ambient pressure, the coefficient γ of the linear T term in the heat capacity shows a rapid increase, and it 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 of intermediate electronic masses to a heavy-fermion state. 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.

Samples were prepared by arc melting the 99.99% metals in an atmosphere of Ar. The ingot was melted several times and then annealed for 5 days at 480 °C. Chemical compositions of the ingots were determined by inductively coupled mass spectrometry. 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. Measurements were performed below 20 K. The magnetic susceptibility was measured in a vibrating sample magnetometer (VSM) in fields up to 9 T with a frequency of 40 Hz. The coefficient of linear thermal expansion α was measured in a three-terminal capacitive dilatometer (see Ref. [26] for details of the apparatus).

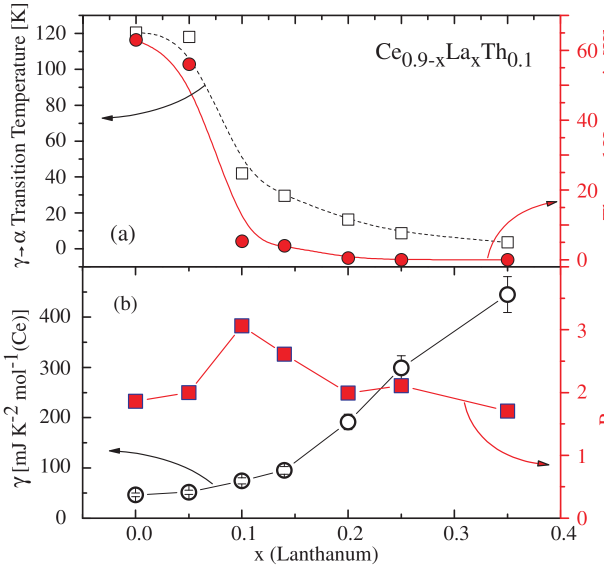

FIG. 1 (color). (a) The effect of alloying on the $\gamma \longrightarrow \alpha$ transition is shown along the left y axis (black), whereas the thermal hysteresis is shown on the right y axis (red). The transition temperature decreases exponentially, and the hysteresis goes to zero (within experimental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

Figure 1(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 50 K at $x < x_c \approx 0.14$ to a line of continuous transitions at $x > x_c$. This result is mirrored in the electronic specific heat and Wilson ratio as shown in Fig. 1(b). Here, a low-temperature heavy Fermi-liquid state develops for concentrations greater than x_c, where the transition temperature of the continuous $\gamma \longrightarrow \alpha$ is close to zero. The Wilson ratio indicates that the heavy Fermi-liquid state does not evolve directly from the α 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 (KW) ratio [27] for $x \leq x_c$ is in agreement with the expected value. For concentrations near x_c, the resistivity varies linearly with T down to 1.9 K, which was the lowest temperature measured. This behavior is frequently found near quantum critical points, and this 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 γ-phase to a temperature-independent susceptibility below the transition. Conversely, for $x = 0.20$ one sees a continuous change with negligible thermal hysteresis $\Delta T \leq 0.5$ K. In the α-Ce phase of this sample,

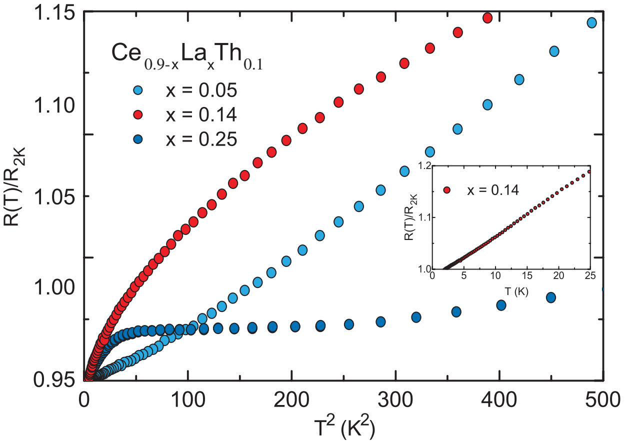

FIG. 2 (color). Temperature variation of the resistivity for concentrations above and below x_c. For convenience, the resistivity is scaled with respect to the resistivity measured at $T = 2$ K, R_{2K}. The inset shows $R(T)/R_{2K}$ as a function of T, for x near x_c.

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].

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) [28,29] for the isomorphous $\gamma \rightarrow \alpha$ transformation in Ce metal. 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 γ^{-1}, we find that in the Fermi-liquid model, the transition is driven by an abrupt change in γ^{-1} over a small range of molar volumes. The cause for an abrupt variation of the Fermi-liquid temperature may be considered outside the scope of the Fermi-liquid model but may be due to the existence of a critical interatomic spacing for Ce [30].

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 ΔE, entropy difference ΔS, volume difference ΔV, 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 300 K to get ΔV and find the remaining three parameters from the data using the Levenberg-Marquardt optimization. In Fig. 4, the volume expansivity, β/T 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

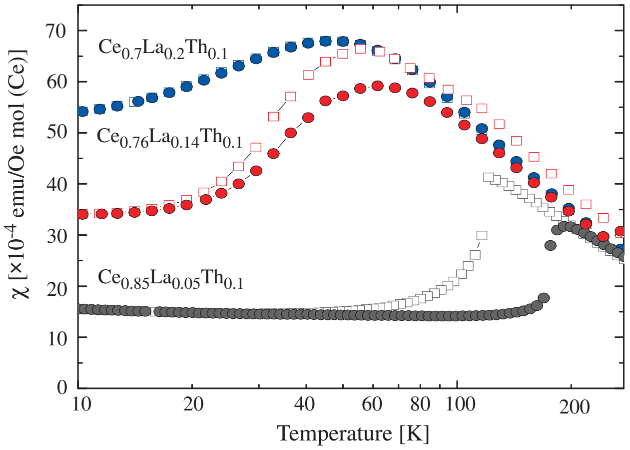

FIG. 3 (color). The magnetic susceptibility as a function of temperature is shown for La concentrations below and above x_c. We note the discontinuous nature of the transition for $x = 0.05$, whereas the transition features a continuous cusp at $x = 0.20$. Also, we note the thermal hysteresis phenomenon present below x_c, disappears above x_c. In order to emphasize the α phase, the transition from Curie-Weiss behavior (high-temperature γ phase) into a Pauli temperature-independent susceptibility is shown on a logarithmic scale. For each concentration, the squares and circles indicate the cooling and warming data, respectively.

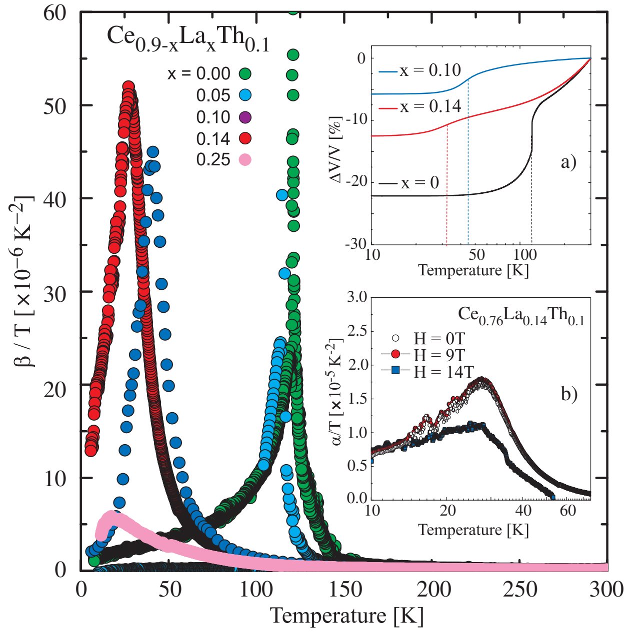

FIG. 4 (color). The $\gamma \rightarrow \alpha$ transition as measured by the thermal expansivity is shown as a function of x in the main figure. Mirroring the susceptibility behavior, the discontinuous nature is apparent at compositions below x_c. Inset (a) shows the evolution of the critical point in $\Delta V/V$, while the magnetic field dependence is shown in inset (b). The critical temperature, T_C, corresponds to the inflection in the $\Delta V/V$ as a function of T curve.

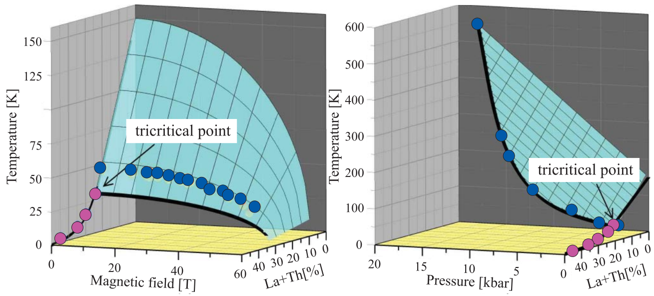

FIG. 5 (color). (a) Three-dimensional phase diagram in temperature, magnetic field, and composition space. A line of critical points suggested by the high magnetic field points (blue) reported here bounds a surface of first-order transitions. (b) Three-dimensional phase diagram in temperature, pressure, and composition space. A line of critical endpoints defined by high-pressure data points (blue) taken from Refs. [22,23] bounds a surface of first-order transitions.

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 $x_c \approx 0.14$ shown by the gentle cusp near 20 K. At this composition, magnetic fields move the phase boundary of the transition in H^2T^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. 5(a). Similarly, combining pressure results from [22] one finds a phase T-p-x diagram shown in Fig. 5(b). 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 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 summary, we have reported the experimental observation of a tricritical point in the phase diagram of $\mathrm{Ce}_{0.9-x}\mathrm{La}_x\mathrm{Th}_{0.1}$ system as a function of the La concentration, x, and we have discussed the resulting phase diagram. The tricritical point is characterized by the thermal hysteresis at the transition going to zero, a transition from intermediate to heavy-electron mass, a peak in the Wilson ratio, a change in the temperature dependence of the resistivity, a change from discontinuous to continuous in the susceptibility, and the thermal expansion, all occurring at $x_c \approx 0.14$. Because Ce systems represent a theoretical testing ground for basic concepts of correlated electron systems, the experimental results presented here are important for the study of phase diagrams in such systems.

This work has been performed under the auspices of the U.S. Department of Energy. We thank R. Hixson and R. Gray for useful discussions.

[1] P. W. Bridgman, *The Physics of High Pressures* (G. Bell and Sons, Ltd., London, 1931).
[2] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 55 (1948).
[3] A. W. Lawson and T.-Y. Tang, Phys. Rev. **76**, 301 (1949).
[4] D. C. Koskenmaki and K. A. Gschneidner, in *Handbook on the Physics and Chemistry of Rare Earth*, edited by K. A. Gschneidner and L. Eyring (North-Holland, Amsterdam, 1978).
[5] D. C. Koskimaki and K. A. Gschneidner, Jr., Phys. Rev. B **11**, 4463 (1975).
[6] L. C. Pauling quoted by A. F. Schuch and J. Sturdivant, J. Chem. Phys. **18**, 145 (1950).
[7] W. H. Z. Zachariasen quoted by A. W. Lawson and T.-Y. Tang, Phys. Rev. **76**, 301 (1949).
[8] D. R. Gustafson, J. D. McNutt, and L. O. Roellig, Phys. Rev. **183**, 435 (1969).
[9] R. F. Gempel, D. R. Gustafson, and J. D. Willenberg, Phys. Rev. B **5**, 2082 (1972).
[10] U. Kornstädt, R. Lässer, and B. Lengeler, Phys. Rev. B **21**, 1898 (1980).
[11] B. Lengeler, G. Materlik, and J. E. Müller, Phys. Rev. B **28**, 2276 (1983).
[12] B. Johansson, Philos. Mag. **30**, 469 (1974).
[13] J. W. Allen *et al.*, Phys. Rev. Lett. **46**, 1100 (1981).
[14] M. Croft, J. H. Weaver, D. J. Peterman, and A. Franciosi, Phys. Rev. Lett. **46**, 1104 (1981).
[15] A. P. Murani, S. J. Levett, and J. W. Taylor, Phys. Rev. Lett. **95**, 256403 (2005).
[16] M. E. Manley *et al.*, Phys. Rev. B **67**, 014103 (2003).
[17] J. W. Allen and R. M. Martin, Phys. Rev. Lett. **49**, 1106 (1982).
[18] I.-K. Jeong *et al.*, Phys. Rev. Lett. **92**, 105702 (2004).
[19] M. E. Manley *et al.*, Phys. Rev. B **65**, 144111 (2002).
[20] M. O. Dzero, L. P. Gor'kov, and A. K. Zvezdin, J. Phys. Condens. Matter **12**, L711 (2000).
[21] F. Drymiotis *et al.*, J. Phys. Condens. Matter **17**, L77 (2005).
[22] J. D. Thompson, Z. Fisk, J. M. Lawrence, J. L. Smith, and R. M. Martin, Phys. Rev. Lett. **50**, 1081 (1983).
[23] J. M. Lawrence, J. D. Thompson, Z. Fisk, J. L. Smith, and B. Batlogg, Phys. Rev. B **29**, 4017 (1984).
[24] G. Eliashberg and H. Capellmann, JETP Lett. **67**, 125 (1998).
[25] M. Dzero, M. R. Norman, I. Paul, C. Pépin, and J. Schmalian, Phys. Rev. Lett. **97**, 185701 (2006).
[26] J. C. Lashley *et al.*, Mater. Trans., JIM **47**, 587 (2006); G. M. Schmiedeshoff *et al.*, cond-mat/0610396 [Rev. Sci. Instrum. (to be published)].
[27] The KW ratio is the ratio of the quadratic term of the resistivity and the linear term of the specific heat. This is found to be constant for transition metals, and for heavy-fermion compounds, respectively. See K. Kadowaki and S. B. Woods, Solid State Commun. **58**, 507 (1986.
[28] I. L. Aptekar' and E. G. Ponyatovsky, Phys. Met. Metallogr. (USSR) **25**, 10 (1968).
[29] I. L. Aptekar' and E. G. Ponyatovsky, Phys. Met. Metallogr. (USSR) **25**, 93 (1968).
[30] H. H. Hill and E. A. Kmetko, J. Phys. F **5**, 1119 (1975).