Two Critical Points on the γ-α Phase Boundary of Cerium Alloys

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(Received 27 December 1982)

It is shown that the P-T diagram for the γ-α phase transition in $Ce_{0.8}La_{0.1}Th_{0.1}$ has two critical points with first-order transitions between them. This phase diagram follows from the Fermi-liquid properties of the $4f$ electronic system, the experimentally known volume dependence of $k_B T_{FL}$, and the dilution effect of alloying.

PACS numbers: 75.40.Dy, 64.70.Kb, 75.20.Hv

The γ-α phase transition in cerium has been extensively studied by pressure and alloying[1]; the line of first-order isomorphic transitions terminates at a critical point in both the x-T and P-T planes. An isomorphic transition also occurs in SmS; and in $Sm_{1-x}R_xS$ alloys (R = Y, Gd), the phase boundary in the x-T plane terminates in two critical points.[1] Similar phase boundaries have also been found in certain liquid-liquid systems in which there is both an upper and a lower consolute temperature.[2] In this paper, we show that in the alloy $Ce_{0.8}La_{0.1}Th_{0.1}$ the phase boundary in the P-T plane terminates in both upper and lower critical points. In general terms, this result follows from the properties of the Fermi liquid formed by the interacting $4f$ electrons. Using the model of Allen and Martin,[3] extended to include the effects of alloying, we calculate a phase diagram in semiquantitative agreement with experiment.

The ($P = 0$, x, T) phase boundary of first-order γ-α transitions in $Ce_{0.9-x}La_xTh_{0.1}$ (Ref. 4) is known[5] to terminate in a critical point ($x_c = 0.09$), beyond which the transitions are continuous. The x-T phase diagram (Fig. 1, inset) was obtained[5] from data such as shown in Fig. 1. The large discontinuities and hysteresis observed for $Ce_{0.9}$-$Th_{0.1}$ in thermodynamic quantities, such as the resistance $R(T)$,[6] progressively shrink with increasing alloy parameter x. For $x > x_c$ continuous, broadened s-shaped curves are observed.

For all alloys studied previously,[5,6] a residual hysteresis (2–3 K) was observed even for $x > x_c$ [Fig. 1 ($x = 0.1$)] and the first-order transitions, especially on warming, were often rounded [Fig. 1 ($x = 0$)]. These effects presumably arise from alloy inhomogeneities and from the inhomogeneous strain fields which accompany the enormous cell collapse ($\Delta V/V \sim 0.15$). Such effects are compounded further in a high-pressure cell by small pressure gradients in the pressure medium (1:1 pentane and isoamyl alcohol) and by pressure changes that occur inevitably when the sample volume changes within the frozen medium.

When pressure is applied to an alloy with $x = 0.10 > x_c$, the sequence exhibited in Fig. 2 is observed. Below 2 kbar, the transitions are s shaped and continuous. At higher pressures (e.g., 4.4 or 6.3 kbar), the transitions are clearly first order: The hysteresis becomes huge ($\simeq$30 K) and a large discontinuity exists between the γ-state and α-state resistances. This effect reaches a maximum near 5 kbar. As pressure is increased further, the discontinuities and hysteresis begin to shrink; and above about 10 kbar, the transitions again take on a continuous character. As a result of the effects mentioned earlier, the first-order transitions are substantially rounded, and hysteresis for continuously transforming samples is larger than at $P = 0$. This makes the critical points difficult to locate pre-

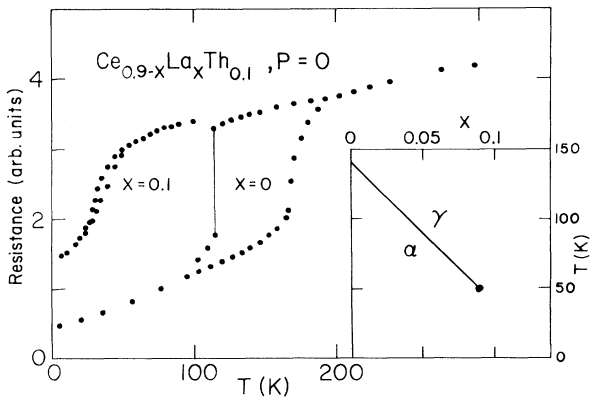

FIG. 1. Resistance vs temperature for $Ce_{0.9}Th_{0.1}$ and $Ce_{0.8}La_{0.1}Th_{0.1}$.

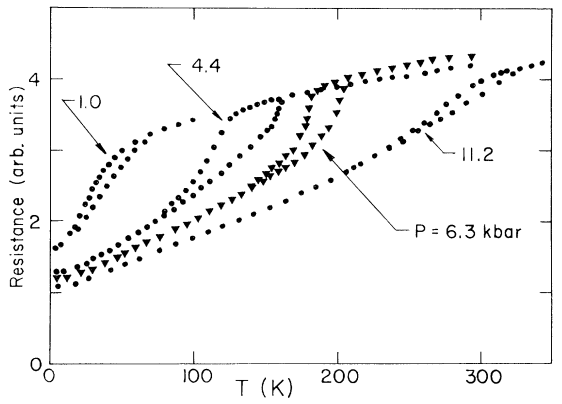

FIG. 2. Resistance vs temperature at four pressures for $Ce_{0.8}La_{0.1}Th_{0.1}$. For clarity we show only ~ 10% of the total number of data points obtained at each pressure. First-order transitions are observed between 3 and 7 kbar.

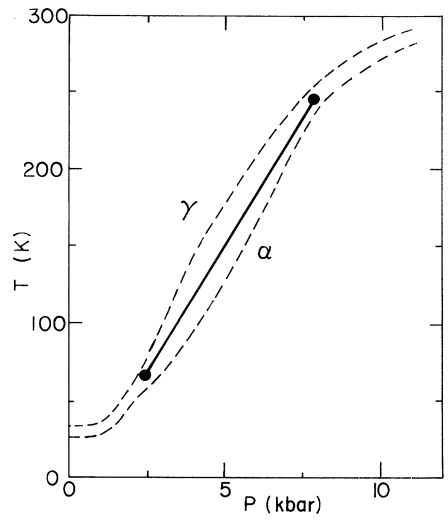

FIG. 3. Experimental P-T phase diagram for $Ce_{0.8}La_{0.1}Th_{0.1}$. The solid line represents the line of first-order transitions, terminating at two critical points. The dashed lines represent the hysteresis, including the residual hysteresis observed for continuous transitions.

cisely. Nevertheless, the actual phase boundary clearly exhibits two critical points. In Fig. 3, we give our best estimate of the phase boundary based on measurements at ten pressures in each of two samples with $x = 0.10$.

To explain this phase diagram, we adopt the following free-energy functional[3,7] for $Ce_{1-x}La_x$:

$$G = (1-x)F^{Ce} + xF^{La} + PV,$$

where

$$F^{Ce} = [\tfrac{1}{2}B_0{}^{Ce}V_0{}^{Ce}][(\overline{V}^{Ce}-1)^2] + E_{FL}(V) - TS_{FL}(T;V)$$

and

$$F^{La} = [\tfrac{1}{2}B_0{}^{La}V_0{}^{La}][(\overline{V}^{La}-1)^2].$$

Here $\overline{V}^{Ce} = V/V_0{}^{Ce}$ and $\overline{V}^{La} = V/V_0{}^{La}$. The "normal" contributions are summarized in the first term of F^{Ce} and in F^{La}. The $4f$ Fermi liquid is represented by a condensation energy E_{FL} and an entropy S_{FL}. It is well known[1,7] that many cerium materials have anomalous thermal expansion and softening described by the above equation. The present work demonstrates the consequences of these Fermi-liquid properties for the γ-α phase transition.

The phase diagram can be understood as follows. At $T = 0$, the bulk modulus for $x = 0$ is

$$B^{Ce}(V;\, T=0) = [B_0{}^{Ce}/V_0{}^{Ce} + \partial^2 E_{FL}/\partial V^2]\,V.$$

The condensation energy is expected to be of order $k_B T_{FL}$. Experimentally this latter is known[8] to vary extremely rapidly with V [approximately[3] as $\exp(-6\overline{V}^6)$]. Over a range of V, then, $\partial^2 E_F/\partial V^2$ can be sufficiently negative to create a negative bulk modulus, i.e., an instability leading to a two-phase region. For pure cerium, this occurs in an inaccessible negative-pressure region.[3] The temperature dependence is determined by the entropy which is a universal function $S(t)$ of scaled temperature $t = T/T_{FL}$. It is a broad s-shaped curve, linear at low temperature, passing through an inflection point near T_{FL}, and saturating to the free-ion $J = \frac{5}{2}$ entropy for $T > T_{FL}$. This saturation leads to the ordinary critical point observed at high temperature. At low temperatures,

$$B(V;\, T) - B(V;\, 0) = -V(1-x)(T^2/T_{FL}{}^3)[(\partial T_{FL}/\partial V)^2\{2S_{FL}{}'(t) + (T/T_{FL})S_{FL}{}''(t)\} - T_{FL}S_{FL}{}'(t)\partial^2 T_{FL}/\partial V^2],$$

which is negative. The term involving $\partial T_{FL}/\partial V$ is always negative, while the one involving $\partial^2 T_{FL}/\partial V^2$ is small for the cases considered below for Ce. This is the important result for the present case: The negative contribution to the bulk modulus *increases* with T for $T < T_{FL}$.

Alloying has two key effects: It dilutes the negative $\partial^2 E_{FL}/\partial V^2$ term causing continuous transitions for large enough x, and it creates a constant pressure shift $xB_0{}^{La}(V_0{}^{La} - V_0{}^{Ce})/V_0{}^{La}$. In the case of lanthanum, this shift is negative, which makes the negative-pressure region accessible. It follows

from the preceding paragraph that the first-order transition will always disappear first at $T=0$, and for some region of lanthanum concentration, the transition will only exist at finite T and P, bounded by lower and upper critical points.

To estimate the critical parameters, the Fermi liquid was modeled as a collection of spin-$\frac{1}{2}$ Kondo impurities.[3] Treating the phase diagram of Ref. 3 as appropriate to $Ce_{0.9}Th_{0.1}$ (i.e., ignoring the effect of thorium dilution), the P-V isotherms and P-T phase boundary were calculated as functions of x. The complete critical behavior is a single line of critical points in x-P-T space occuring only for $x \leq 0.16$. This line makes two intersections with those P-T planes having $0.09 \lesssim x \lesssim 0.16$. The results for $x=0.10$ and $x=0.16$ are shown in Fig. 4. For $x=0.10$, the critical points are predicted at 1.4 kbar, 60 K, and 7.8 kbar, 400 K, in good agreement with experiment. Another prediction is that for $x=0.16$, the two critical points coalesce to form a critical inflection point and that for $x>0.16$ all transitions are continuous. Our data (not shown) for $x=0.11$ indicate that both critical points still exist for that concentration; but preliminary cooling data suggest that the first-order transitions with pressure are already completely absent for $x=0.14$. Despite the simplifying aspects of the theory, we feel it captures the essential experimental results.

The qualitative aspects of the phase diagram are seen to follow from rather general properties of the Fermi liquid [the universality of $S_{FL}(T/T_{FL})$, the strongly nonlinear volume dependence of $E_{FL}(V)$] as well as from low-order alloying effects (dilution of the interaction and negative pressure). On the theoretical side, this suggests that a number of models for cerium might be able to duplicate these results, although whether other models *can* give as good agreement with the observed phase diagram is not known *a priori*. The microscopic origin of the Fermi liquid as well as of the volume dependence of T_{FL} is an open question that cannot be resolved by the phase-diagram data alone (indeed the microscopics may differ in different systems), and the appropriateness of any particular model, such as the Anderson lattice in the Kondo regime, relies on its ability to encompass other properties, such as f occupation, low-energy magnetic fluctuations, photoemission, bremsstrahlung isochromat spectroscopy measurements, etc.

Experimentally, we expect such a phase diagram for other alloys $Ce_{1-x}R_x$ with $V_0^R > V_0^{Ce}$ [e.g., R = Yb, Eu (Ref. 5)] since this is the condition required to make the negative-pressure region accessible. That the observation of two critical points is nontrivial can be seen from the fact that in the only other case studied to date (Ce_{1-x}-Th_x) the effect is not observed. The line of critical points $P_c(x)$, $T_c(x)$ extending from the $x=0$, P-T plane to the $P=0$, x-T plane is nearly linear and $P_c(x)$ is nowhere double valued.[9] In the case of $Sm_{1-x}R_xS$ alloys, it is not known experimentally whether two critical points exist in any P-T plane at fixed x. The physics, while related to that of cerium, is not identical. One similarity is that the low-temperature critical point in the $P=0$ plane (x_c^L, T_c^L) arises in both cases primarily from a simple dilution of the nonlinear interactions responsible for the first-order transitions. An important difference is that, for the case of SmS alloys, the ground state for x close to x_c^L is not, on the face of it, expected to be a Fermi liquid, but rather a divalent $J=0$ singlet. Hence, it is not simple to generalize from the present results to the SmS case.

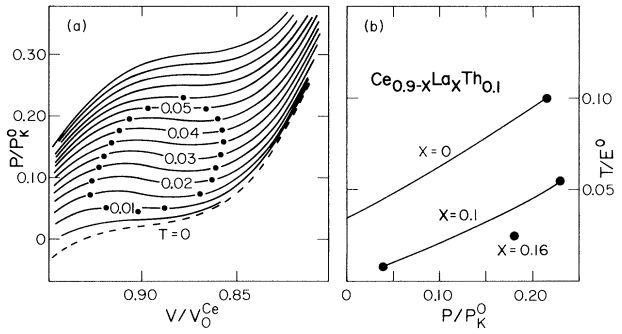

FIG. 4. (a) Calculated P-V isotherms for $Ce_{0.8}La_{0.1}$-$Th_{0.1}$. Units are such that $T=0.04$ corresponds to 300 K, $V_0^{Ce}=36$ Å (Ref. 3), and $P_K^0=34$ kbar. The solid dots represent the points of phase equilibria. (b) The calculated P-T phase boundaries for $Ce_{0.9-x}La_xTh_{0.1}$. For $x=0.16$, the two critical points coalesce; for $x>0.16$, only continuous transitions are expected.

We wish to thank J. W. Allen and Conyers Herring for very useful discussions and K. C. Lim for automating the data acquisition. The work at Los Alamos National Laboratory was performed under the auspices of the U. S. Department of Energy.

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