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Phase diagram and critical points of Ce alloys (invited)

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The pressure-temperature phase diagram of $\text{Ce}_{0.9-x}\text{La}_x\text{Th}_{0.10}$ alloys is presented for $0.1 \leq x \leq 0.17$. Two critical points are found in this range of compositions. The data are shown to be consistent with an analysis based on the known Fermi-liquid behavior of Ce in compounds and alloys. The possible appearance of β phase at intermediate pressures is noted.

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The pressure-temperature (P-T) phase diagram of Ce is unique among the elements in that it possesses a phase boundary (the $\gamma - \alpha$ boundary) ending in a critical point (Fig. 1).¹ The large volume collapse ($\sim 15\%$) across this boundary is generally agreed to be connected with the $4f$ electrons of Ce; however, the nature of this connection is a strongly disputed subject. The one point on which there is agreement is that in the ground state the $4f$ -electronic system of cerium can be described as a Fermi liquid,² as clearly evidenced by the enhanced Pauli paramagnetism and linear specific heat coefficient. This situation also holds for many nonmagnetic Ce intermetallics. A high level of universality exists among these compounds: properties such as magnetic susceptibility, effective moment, etc., scale with a characteristic Fermi-liquid temperature (T_{FL}) even with T_{FL} varying over a large range (1–1000 K). In addition the $4f$ -spin degrees of freedom are quenched in the Pauli paramagnetic state. It is on the question of the microscopic character of this Fermi liquid that no real agreement exists.

The experiments to be described address the question of what sort of phase diagram might be observed for Ce if negative pressures were accessible. Alloying experiments show that in $\text{Ce}_{0.9}\text{Th}_{0.1}$, the β phase is entirely suppressed.³ Because of its smaller atomic volume, Th acts roughly as a positive pressure on the Ce lattice. Addition of La to $\text{Ce}_{0.9}\text{Th}_{0.1}$ depresses the $\gamma - \alpha$ transition⁴ as shown in the inset to Fig. 2. Beyond a critical lanthanum concentration ($x = 0.09$) in $\text{Ce}_{0.9-x}\text{La}_x\text{Th}_{0.10}$, the $\gamma - \alpha$ transition is continuous at ambient pressure. The atomic volume of La is larger than $\gamma - \text{Ce}$, and La acts, in this alloy, in some sense as a negative pressure would, in addition to being a diluent of the Fermi-liquid interactions. The point is that one might expect a second critical point in the negative pressure region, on the basis of these La alloying results.

It is possible to track the $\gamma - \alpha$ transition using electrical resistivity measurements. Figure 2 shows data at $P = 0$ for samples in both the first-order and continuous regimes. Other studies have shown that the change in electrical resistivity in the critical region is proportional to the volume change.³ A complicating feature in the analysis of the data is the presence of a small 2–3 K residual hysteresis, even for samples that exhibit continuous transitions. This can be seen in the $x = 0.1$ data of Fig. 2, and also contributes to the rounding of the warming transition for $x = 0$. We believe this is due to compositional variations in the alloy. The situation is exacerbated in high pressure measurements by nonhydrostatic

stresses induced in the solid pressure medium during the enormous volume change at the transition.

We show our data for $\text{Ce}_{0.80}\text{La}_{0.10}\text{Th}_{0.10}$ in Fig. 3. (Experimental details will appear elsewhere.) We can clearly see the hysteresis broaden and then contract as a function of pressure. In addition, the shape of the hysteresis curve changes dramatically. Combining these data with our results for $x = 0.11, 0.14$, and 0.17 , we construct the phase diagrams of Fig. 4. While it is difficult to place the critical points exactly because of problems mentioned above, we believe there is a clear case for the existence of two critical points in the range $0.10 \leq x \leq 0.14$. We see from the composite phase diagrams in Fig. 4(c) that as the lanthanum concentration increases, the two critical points move together until for $x = 0.17$ there is no evidence for a first-order transition at any part studied. Therefore, at some critical concentration the two critical points coalesce to form a "critical inflection" point. We estimate this critical concentration to be $x = 0.16$.

FIG. 1. $P - T$ phase diagram for Ce (from Ref. 1).

FIG. 2. Resistance vs temperature for $\text{Ce}_{0.9-x}\text{La}_x\text{Th}_{0.1}$ and $\text{Ce}_{0.8}\text{La}_{0.1}\text{Th}_{0.1}$. The $x-T, P=0$ phase diagram for the $\gamma-\alpha$ transition in $\text{Ce}_{0.9-x}\text{La}_x\text{Th}_{0.1}$ is shown in the inset (from Ref. 4).

It is interesting to investigate the requirements of a theory needed to explain the phase diagram.⁵⁻⁷ Consider an alloy $\text{Ce}_{x-1}\text{La}_x$, ignoring the complications of a third component which do not substantially alter the argument. We write the free-energy functional as

$$G = (1-x)F^{\text{Ce}}(V) + xF^{\text{La}}(V) + PV, \quad (1a)$$

FIG. 3. Resistance vs temperature for $\text{Ce}_{0.80}\text{La}_{0.10}\text{Th}_{0.10}$ at several clamp pressures. The curves are displaced vertically for clarity.

FIG. 4. Pressure-temperature phase diagrams for $\text{Ce}_{0.9-x}\text{La}_x\text{Th}_{0.1}$ with $x=0.10$ (a) and $x=0.14$ (b). The small dots give the values of P and T for the warming and cooling transitions, and the solid lines are our estimate of the equilibrium phase boundary of first-order transitions with their termination in critical points (large solid circles). The dashed lines represent the locations of the continuous transitions. The equilibrium boundaries are plotted together in (c) together with our $x=0$ and $x=0.17$ data. The open circle in (c) gives our estimate of the parameters of the "critical inflection point."

where

$$F^{\text{La}} = \frac{1}{2}B_0^{\text{La}}V_0^{\text{La}}(V/V_0^{\text{La}} - 1)^2, \quad (1b)$$

and

$$F^{\text{Ce}} = \frac{1}{2}B_0^{\text{Ce}}V_0^{\text{Ce}}(V/V_0^{\text{Ce}} - 1)^2 + F_{\text{FL}}(T, V). \quad (1c)$$

Except for the last term in Eq. (1c), this free energy is that of a simple mixture in the approximation that every atom in the

alloy possesses the same average volume V . The normal volume V_0^{La} and bulk modulus B_0^{La} are those for fcc La. The corresponding quantities for Ce are obtained by smooth interpolation between La and Pr: $V_0^{\text{Ce}} = 36 \text{ \AA}^3$, $B_0^{\text{Ce}} = 280 \text{ kbar}$.

The anomalous terms which drive the phase transition are contained in F_{FL} . The transition is viewed as occurring between the α -state with $T_{\text{FL}} \approx 1000 \text{ K}$ and the γ state with $T_{\text{FL}} \approx 100 \text{ K}$, as suggested by inelastic neutron scattering experiments.^{8,9} The temperature dependence of F_{FL} is determined by the entropy of the Fermi liquid. This is known to scale with T_{FL} : S_{FL} is a universal function of the scaled temperature $t = T/T_{\text{FL}}$, and $S_{\text{FL}}(T; V) = S_{\text{FL}}[T/T_{\text{FL}}(V)]$.⁹

The free energy F_{FL} , therefore, has the form

$$F_{\text{FL}}(T; V) = E_{\text{FL}}^0(V) - T f[T/T_{\text{FL}}(V)], \quad (2a)$$

where

$$f(t) = \frac{1}{t} \int_0^t S(t') dt'. \quad (2b)$$

The condensation energy E_{FL}^0 is expected to be of order $k_B T_{\text{FL}}(V)$, which is known from experiment to be a strongly nonlinear function of the cell volume.⁵ It is this nonlinearity which drives the first-order collapse.

The appropriate equation of state is obtained by mini-

mizing G with respect to volume at constant T and P . For pure Ce ($x = 0$) this gives

$$0 = \frac{\partial G}{\partial V} = P + \frac{B_0^{\text{Ce}}}{V_0^{\text{Ce}}} (V - V_0^{\text{Ce}}) + \frac{\partial E_{\text{FL}}^0}{\partial V} + \frac{T^2 f'_{\text{FL}}}{T_{\text{FL}}^2} \frac{\partial T_{\text{FL}}}{\partial V}, \quad (3)$$

where f'_{FL} is the derivative of f_{FL} with respect to the scale variable t . This equation of state is examined for negative values of the bulk modulus $B = -V(\partial P/\partial V)$. For this, we need $S(T/T_{\text{FL}})$ and $T_{\text{FL}}(V)$. These can be estimated from respectively the effective moment of Ce in compounds⁹⁻¹¹ and inelastic neutron scattering for Ce alloys, as discussed further elsewhere.⁷ We also make the crude approximation that $E_{\text{FL}}^0 = -k_B T_{\text{FL}}$.

$S(t)$ and $T_{\text{FL}}(V)$ are plotted in Figs. 5(a) and 5(b). In Fig. 5(c) we show $\partial k_B T_{\text{FL}}/\partial V$ obtained by numerically differentiating T_{FL} [Fig. 5(b)] and the $P - V, T = 0$ isotherm for "normal" Ce. Curve 1 in Fig. 5(c) represents the sum of these two terms and shows that the $\gamma - \alpha$ transition occurs at negative pressure ($P \approx -5 \text{ kbar}$). The effect of increasing T is

FIG. 5. (a) Entropy as a function of scaled temperature $t = T/T_{\text{FL}}$ for Ce compounds. T_{FL} is the Fermi-liquid temperature. (b) Characteristic temperatures T_{FL} as a function of volume per atom for Ce alloys. The points are estimates of T_{FL} using inelastic neutron scattering line width data (Refs. 8 and 12). The smooth line is our interpolation. The dashed line is a plot of the First term on the right side of Eq. (1c). (c) Dashed lines represent separately the sum of the "normal" $P-V$ isotherm and the term $-\partial k_B T_{\text{FL}}/\partial V$. Curve 1 is the sum of these two terms. Curve 2 represents qualitatively the change in shape of the isotherm at low temperatures. Curve 3 represents a critical isotherm obtained from curve 1 by either raising temperature or by alloying at $T = 0$. Curve 4 represents the result of first alloying (so as to obtain curve 3 at $T = 0$) and then raising the temperature.

FIG. 6. Resistance vs temperature (upper block) for $\text{Ce}_{0.8}\text{La}_{0.1}\text{Th}_{0.1}$ at $P = 8.3 \text{ kbar}$. The anomalously large increase in the resistance near 200 K may signal the appearance of β -Ce which remains stabilized to 4 K . The lower block shows that the resistance of this phase follows a T^2 dependence over a large temperature interval.

shown qualitatively in the progression of curves 1→3, the high temperature critical point corresponding to isotherm 3.

For $x \neq 0$, we have

$$P = (1-x)P^{\text{Ce}}(V) + x(B_0^{\text{La}}/V_0^{\text{La}})(V_0^{\text{Ce}} - V) + x(B_0^{\text{Ce}}/V_0^{\text{La}})(V_0^{\text{La}} - V_0^{\text{Ce}}), \quad (4)$$

where $P^{\text{Ce}}(V)$ is the P - V equation of state for pure Ce [Eq. (3)]. The effect of alloying is then a constant pressure shift [the last term in Eq. (4)] making part of the negative pressure region accessible, and a dilution of the Fermi-liquid terms. There will be a critical concentration such that the $T=0$ isotherm will resemble curve 3 in Fig. 5(c), but which, as T is increased, will develop into curve 4. This gives a lower critical point at positive pressure. The essential point is that this treatment only depends on experimentally established Fermi-liquid behavior. At the same time, we note that this behavior was originally predicted by the calculations of Allen and Martin⁵ based on a Kondo model.

There is a further interesting point connected with the 7.3 kbar warming curve in Fig. 3. We believe another phase started growing in at ≈ 190 K, the most likely candidate being the β - $dhcp$ phase. We saw further much more pronounced evidence for this in other cool downs, including the occurrence of this phase, stable all the way to 4 K in one run. (See Fig. 6.) In the picture introduced, that alloying with La is in some ways similar to negative pressure, the occurrence of the phase might indeed be expected because of reduction

of the effects of the Th at some pressure intermediate between the critical points.

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