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Valence Transition in Chemically Collapsed Cerium

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(Received 21 August 1978; revised manuscript received 8 January 1979)

The scaling behavior of the Landau equation of state which describes the valence transition in cerium is studied as a function of the size and valence of various chemical additives. Two major results are the relatively direct determination of the valence N of cerium at the critical point (viz., $N=3.65$) and the finding that the presence of chemical additives leads to a lattice-mediated rather than Coulombic bootstrapping term, which addresses the long-standing question of what is the driving mechanism for the valence transition.

Cerium, being the only chemical element known to undergo (in the fcc phase) a valence transition with temperature, has been studied extensively during the past two decades, and is a primary archetype of so-called Anderson lattice systems. These systems, whose unusual behavior results from the close proximity of a localized (usually $4f$) level to the Fermi level, exhibit a variety of interesting many-body phenomena.[1] These include valence transitions (e.g., Ce or SmS), mixed (nonintegral) valence (e.g., Ce, SmS, or $CePd_3$), and exotic magnetically ordered states (e.g., $CeAl_2$) characterized by spatial modulations in both the magnitude and direction of the moments.

The valence of an Anderson lattice in the mixed-valence state reflects the degree of hybridization of the local state with the conduction-electron state.[2] Of the various experimental approaches used previously to determine (mixed) valence, the measurement of lattice constant is the most straightforward. Implicit in the practical utilization of this method is (1) the assumption of a linear (or some other) relationship between the lattice constant and the (mixed) valence and (2) a knowledge of the lattice constants for the two integral valence values which bracket the mixed valence. The present study, which yields the valence of cerium at the critical point of the chemically induced valence transition, focuses on the scaling properties for different chemical additives of the Landau equation of state which describes the valence transition. This equation, which was shown previously[3,4] to be valid for $Ce_{1-x}Th_x$ in a relatively large region of x-T space encompassing the critical point ($x_0=0.265$, $T_0=148$ K), where x plays effectively the role of the pressure, is of the form

$$\delta T = a(\delta\rho)^3 + b\,\delta x\,\delta\rho + c\,\delta x, \qquad (1)$$

where the dimensionless quantities δT, δx, and $\delta\rho$ (resistivity) are all scaled to their critical values, e.g., $\delta T=(T-T_0)/T_0$. Since it was established previously[3,4] that the electrical resistivity couples linearly to the order parameter, viz., $\langle n_{4f}\rangle$, the average occupancy of the local level, we are justified in using the above form for the equation of state.

The alloy systems studied were $Ce_{0.9-x}X_xTh_{0.1}$ with X = Th, Sc, La, Eu, Gd, Dy, Er, Yb, and Lu. 10% Th was present in all samples to suppress the formation of hexagonal β-phase cerium. Figure 1 exhibits the valence-transition coexistence curves for the various additives. The locus of transitions represents, from left to right, first-order transitions, terminating in a critical point (x_0, T_0), followed by weaker transitions. In all of the systems studied, the coexistence curves were approximately linear in the concentration range $0 \leq x \leq x_0$. In Fig. 2 the slope of the coexistence curves is plotted versus the fcc metallic radius of the additive. Fitting the data for the trivalent additives (Sc, Lu, Er, Dy, Gd, and La) by a straight line and assuming an arbitrary dependence $f(N)$ of dT_c/dx on the valence N of the additive results in

$$\Delta T_c/\Delta x = -69(R-R_0)/R_0 + f(N), \qquad (2)$$

where for reasons given below we have chosen $R_0 = 1.746$ Å. Plotting $F(N) = dT_c/dx + 69(R-R_0)/R_0$ versus N in Fig. 3, with $N = 4$ for Th and $N = 2$ for Eu and Yb, yields to a good approximation a linear dependence of $f(N)$ on N. This allows us to reexpress Eq. (2) as

$$\frac{T_c}{x} = -69\frac{R-R_0}{R_0} + 24\frac{N-N_0}{N_0}, \qquad (3)$$

with $N_0 = 3.65$, corresponding empirically, and as we shall discuss below, to the valence of Ce at the critical point.

The behavior of the coefficient $c \equiv (x_0/T_0)\Delta T_c/\Delta x$ in Eq. (1) is explicitly expressed in Eq. (3). The behavior of the coefficients a and b were determined from studies of $\rho(T)$ for $x > x_0$, i.e., in the region of nonsingular transitions. The behavior of a and b is shown in Fig. 4. To within experimental uncertainty a is *independent of both R and N*, having the value $a = 0.52$. On the other hand, the parameter b is *independent of N*, but depends *strongly (and approximately linearly) on R*. Extrapolation of $b(R)$ to $b = 0$ provides the motivation for choosing the fiducial radius $R_0 = 1.746$ Å.

We shall discuss first the implications of this work on the question of driving mechanisms for the valence transition, and then return to the question of the valence of cerium. First, we note that the third term on the right-hand side of Eq. (1), which expresses a renormalization of T_0 and is not a bootstrapping term, depends equally strongly on the valence and the metallic radius of the ternary additive. As discussed previously[6] in a report on the early phase of this work, we interpret the observed behavior of the coefficient c to imply that the dominant size effect is to simulate either positive or negative pressure, thereby moving the $4f$ level with respect to the Fermi level. On the other hand the results seem to imply[6] that the dominant valence effect (referring to the ternary additive) is basically a Coulombic (or screening) effect which can both alter the width of the $4f$ level and change its energy with respect

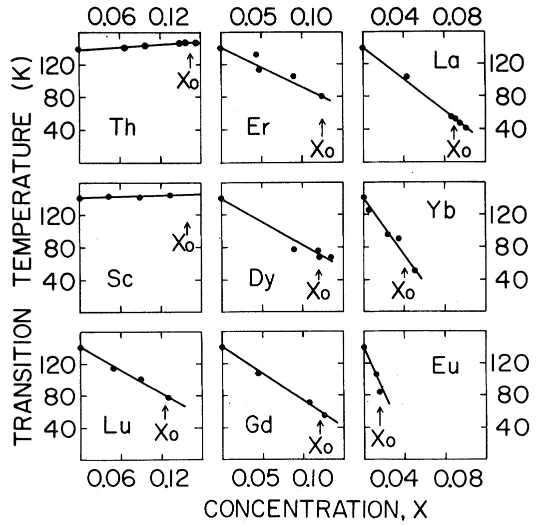

FIG. 1. Valence-transition temperature vs concentration x of the ternary additive X for the system $Ce_{0.9-x}X_xTh_{0.1}$. The critical concentration x_0 is denoted by arrows.

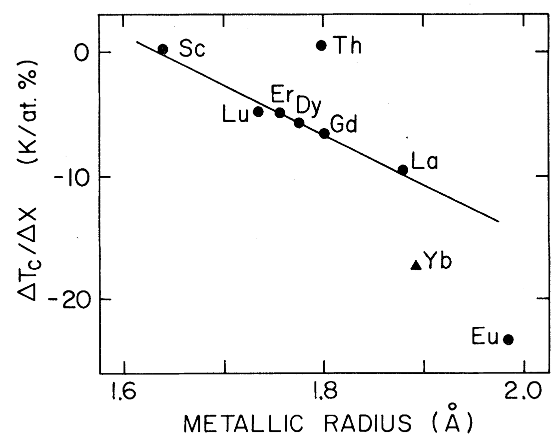

FIG. 2. Slope of coexistence curves $\Delta T_c/\Delta x$ (see Fig. 1) vs metallic radius of the ternary additive.

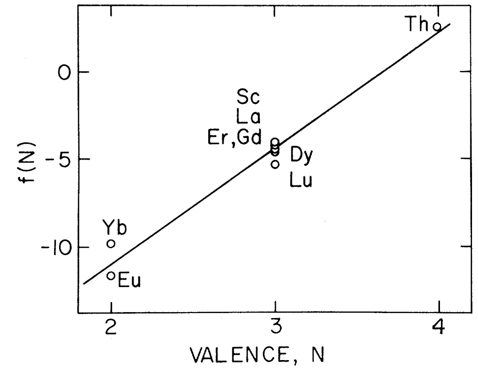

FIG. 3. Function $f(N)$, defined in text, vs valence N of the ternary additive.

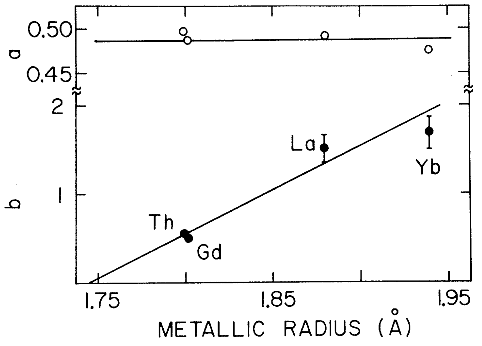

FIG. 4. Dependence of parameters a and b of the Landau equation of state [Eq. (1)] on the metallic radius of the ternary additive.

to the Fermi level. Since the (bootstrapping) second term on the right-hand side of Eq. (1) depends on the size but not on the valence of the additive, we look to lattice effects as the source of the driving mechanism. Among lattice-related effects, it would seem to be difficult, based on the present results, to choose between band deformation effects induced by lattice deformations[7,8] or acoustic strain effects[9] as relevant to the problem of phase separation in alloys.

Making contact with the popular wisdom on the valence of fcc (α and γ) cerium, we refer to the often-quoted work of Gschneidner and Smoluchowski.[10] They arrive at the following valence values for cerium, based upon lattice-constant measurements: (a) $N=3.72$ for α-Ce at $T=116$ K (just below the temperature-induced valence transition), (b) $N=3.49$ for α-Ce at $P=7670$ Torr and $T=296$ K, and (c) $N=3.26$ for fcc cerium at the critical point, $P=24\,800$ Torr and $T=695$ K (here the α and γ phases are one). A number of approximations are folded into these estimates, viz., (1) an estimated value for the metallic radius of hypothetical tetravalent ($N=4$) cerium, (2) an assumed linear dependence of valence on metallic radius in the entire concentration range $3 \leq N \leq 4$, (3) thermal-expansion corrections for (a) and compressibility corrections for (b), and (4) pertaining only to (c), the *ad hoc* assumption that N depends linearly on pressure and temperature.

The procedure reported herein yields the value $N=3.65$ for cerium at the chemically induced critical point for a number of Ce-based systems. This method requires no approximations of the nature of those listed above, but rather, only the assertion that the fiducial quantity N_0 in Eq. (5) is in fact the valence of cerium at the critical point. Invoking the popular but *ad hoc* assumption that valence couples linearly to volume over the entire valence range $3 \leq N \leq 4$, and using the fiducial value $R_0 = 1.746$ Å, together with the endpoint values $R_{N=3} = 1.846$ Å and $R_{N=4} = 1.672$ Å (after Ref. 10), yields $N=3.60$, which is somewhat lower than the fiducial value $N_0 = 3.65$. However, this is within our estimated uncertainty of ± 0.05 in N_0, so that we cannot challenge the linear coupling hypothesis on the basis of the present results.

The relatively large value of N at the critical point, which should be significantly smaller than that in the totally collapsed phase (viewing the critical point as roughly the midpoint between the two phases) allows the speculation that the low-temperature ($T \to 0$) ground state of α-Ce might be fully tetravalent ($N=4$) rather than mixed valent as is commonly thought. Indeed, the enhancement factors observed[11] in the low-temperature specific heat and magnetic susceptibility of α-Ce, both with respect to their size and ratio, agree less well[12] with current theory[13] than in the case of other mixed-valent systems, e.g., $CePd_3$, $YbAl_3$, and YbCuAl. If α-Ce is, in fact, integral valent at low temperatures, then the enhancement factors observed might reflect the presence of virtual excitations to the $4f$ level, which, in that situation, would lie just above the Fermi level.

The authors are particularly grateful to Professor K. A. Gschneidner, Jr., for critically reading this manuscript and providing currently accepted values for the various metallic radii required in the analysis. This work was supported in part by the Office of Naval Research and the

Army Research Office. A more complete report will be published elsewhere.

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Universal Current Scaling in the Critical Region of a Two-Dimensional Superconducting Phase Transition

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(Received 31 October 1978)

The transition to a superconducting state in ultrathin (~30 Å) granular niobium nitride is found to obey scaling laws characteristic of critical regions near phase transitions. Dynamic scaling of voltage with current is theoretically suggested in analogy with magnetic phase transitions and is experimentally demonstrated. A universal function of current and temperature involving two independent critical exponents is generated.

Critical phenomena have been of great interest for many years. Unfortunately, methods developed for studying the critical region of a phase transition are not readily applicable to the usual bulk superconducting transition because of experimental difficulties in exploring the very narrow critical region ($<10^{-6}$ K). Recently, unusually broad transitions to the superconducting state have been observed in granular- and ultrathin-film systems, suggesting that a superconducting critical region may be experimentally accessible in these materials.[1-6] This Letter reports the first demonstration of universal current scaling in the critical region for a superconducting transition of two-dimensioanl (2D) granular NbN films. It is shown that the dynamic variable voltage V can be expressed in terms of a universal function of current I and temperature T involving two independent critical exponents.

The recognition that voltage near a superconducting transition should scale with current and temperature arises by analogy to other critical phenomena.[7-9] The zero-field magnetic susceptibility χ of an Ising ferromagnet, for example, diverges as T approaches the critical temperature T_c from above like $\chi \equiv [\partial M/\partial H]_{H=0} \propto (T-T_c)^{-\gamma}$, where M is the magnetization and H is the magnetic field. While the zero-field χ is infinite at T_c, the finite-field χ is not. Thus at T_c, $M(H)$ is not a linear function, i.e., $H \propto M^{\delta}$ where $\delta > 1$. More generally, $M(H, T-T_c)$ satisfies a well-known scaling equation of state. By analogy, the electrical conductivity $\sigma \equiv [\partial j/\partial E]_{E=0}$ (j is the current density and E the electric field) is infinite at the superconducting T_c only for $E=0$, e.g., $\sigma \propto (T-T_c)^{-\mu}$.