



# Insensitivity of the pressure dependences of characteristic energy scales in $\text{Ce}_{1-x}\text{R}_x\text{CoIn}_5$ ( $R = \text{Yb}, \text{Y}, \text{Gd}$ ) to the electronic configuration of the rare-earth ion

B. D. White, J. J. Hamlin, K. Huang, L. Shu,<sup>\*</sup> I. K. Lum, R. E. Baumbach,<sup>†</sup> M. Janoschek,<sup>†</sup> and M. B. Maple  
*Department of Physics, University of California, San Diego, La Jolla, California 92093, USA*

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Cooperative Ce and Yb valence fluctuations have recently been proposed as the mechanism responsible for stabilizing correlated electron phenomena in  $\text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5$  over an unexpectedly large range of concentrations. In order to better understand the origins and character of this stability, we have measured the effect of applied pressure on relevant energy scales such as the superconducting critical ( $T_c$ ) and Kondo-lattice coherence ( $T^*$ ) temperatures of  $\text{Ce}_{1-x}\text{R}_x\text{CoIn}_5$  with  $R = \text{Yb}, \text{Y},$  and  $\text{Gd}$ . Electrical resistivity measurements were performed under applied pressure on samples doped with intermediate-valent Yb and stable-valent Gd and Y, and the responses of  $T_c$  and  $T^*$  to increased pressure in these systems are compared. The character of  $T_c(P)$  and  $T^*(P)$  in  $\text{Ce}_{1-x}\text{R}_x\text{CoIn}_5$  depends only on their respective ambient-pressure values  $T_c(0)$  and  $T^*(0)$ , independent of the electronic configuration of  $R$  or concentration  $x$ . The consequences of this result are discussed within the context of possible cooperative valence fluctuations in  $\text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5$ .

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## I. INTRODUCTION

A rich variety of strongly correlated electron phenomena have been observed in the superconducting and normal states of  $\text{CeCoIn}_5$ , which continue to attract significant experimental and theoretical interest.<sup>1,2</sup> Critical fluctuations associated with this system's close proximity to an antiferromagnetic quantum critical point (QCP) are thought to provide a mechanism for both non-Fermi-liquid (NFL) metallic states and unconventional  $d$ -wave superconductivity (SC) near  $T_c = 2.3$  K.<sup>3</sup> These properties naturally emerge from the delicate interplay of structural optimization and hybridization between localized  $f$  electrons and itinerant conduction electrons. The relationship between quantum criticality, NFL behavior, and unconventional SC continues to play a central role in the study of the "115" systems and potentially has broader relevance to strongly correlated electron physics in general.<sup>4,5</sup>

Recent studies of the system  $\text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5$  have demonstrated that Yb substitution provides a useful tuning parameter for exploring quantum critical (QC) phenomena in  $\text{CeCoIn}_5$ .<sup>6,7</sup> These studies were primarily motivated by the observation in  $\text{Ce}_{1-x}\text{R}_x\text{CoIn}_5$  ( $R =$  rare earth) that Cooper pair breaking and Kondo-lattice coherence are uniformly influenced as a function of  $x$ , independent of the electronic configuration of the substituent  $R$ , while NFL behavior depends strongly on the  $f$ -electron configuration of  $R$  ions.<sup>8</sup> In marked contrast to these observations, many of the correlated electron phenomena which are characteristic of  $\text{CeCoIn}_5$  are only weakly affected by Yb substitution. For example, the suppression of  $T_c$  with  $x$  extrapolates to zero temperature only near  $x = 1$ .<sup>6</sup> This result is remarkable considering that other rare-earth ion substitutions in  $\text{Ce}_{1-x}\text{R}_x\text{CoIn}_5$  suppress SC by  $x \sim 0.25$ .<sup>8</sup> It is interesting to note that recent measurements on thin films of  $\text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5$  reveal a more rapid suppression of  $T_c$  than seen in bulk samples;<sup>9</sup> however,  $T_c$  vanishes near  $x = 0.4$ , which is still roughly a factor of 2 higher than in bulk samples containing other rare-earth ions. This difference in behavior between thin-film and bulk Yb-doped samples might arise from the nonequilibrium nature of molecular-beam epitaxy.

Three energy scales collectively characterize the Ce-based Kondo lattice in  $\text{CeCoIn}_5$ : the single-ion Kondo temperature  $T_K$ , the Kondo-lattice coherence temperature  $T^*$ , and the crystalline electric field (CEF) splitting of the Ce  $J = 5/2$  multiplet.<sup>10,11</sup>  $T^*$  is typically identified with the maximum in electrical resistivity  $\rho$  near 40 K and depends only weakly on  $x$  in  $\text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5$  throughout the concentration range where single-phase samples can be synthesized.<sup>6</sup> As a consequence, the scaling between  $T_c$  and  $T^*$ , which is typically observed in heavy-fermion SC compounds, appears to be violated.<sup>12</sup> In fact, if the conventional interpretation is incorrect and the maximum in  $\rho$  is a consequence of CEF effects, then there is no reason to expect this scaling to work.

The mechanism responsible for these unanticipated observations is not yet confirmed; however, several ideas have recently been proposed.<sup>6,13,14</sup> One proposal envisions a Kondo lattice in which Ce and Yb ions adopt cooperative intermediate-valence states whereby Yb ions mimic the electronic configuration of Ce ions.<sup>6</sup> In the context of such a scenario, it might be expected that Yb substitution would perturb the Kondo lattice in  $\text{CeCoIn}_5$  more weakly than would introduction of other rare-earth ions with stable valences. Recent angle-resolved photoemission spectroscopy, extended x-ray absorption fine structure, and x-ray absorption near-edge structure measurements on  $\text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5$  samples observe a strongly intermediate-valence state of  $\text{Yb}^{2.3+}$  for most Yb concentrations.<sup>13,15</sup> For  $x \leq 0.2$ , the Yb valence suddenly and continuously increases to a nearly trivalent state at the lowest Yb concentrations.<sup>15</sup> The Ce valence in this system remains nearly trivalent for all  $x$ .<sup>13,15</sup> A second proposal suggests that the stability of correlated electron phenomena in  $\text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5$  originates with details concerning the microstructure of synthesized samples. Booth *et al.* suggest in Ref. 13 that, below a concentration  $x_{PS}$  where macroscopic phase separation in  $\text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5$  occurs, interlaced networks of  $\text{CeCoIn}_5$  and  $\text{YbCoIn}_5$  coexist, and that  $\text{YbCoIn}_5$  networks may have a weak collective effect on the physical properties of  $\text{CeCoIn}_5$  networks. In this scenario, intermediate-valent Yb ions in  $\text{YbCoIn}_5$  influence

the local electronic density as well as  $T_K$  for the neighboring  $\text{CeCoIn}_5$  networks, the result of which is to systematically lower  $T_c$  in those networks.<sup>13</sup> To date, no direct probe has provided any compelling evidence for the existence of these networks. Finally, a Kondo disorder model, wherein correlations between Yb ions were studied theoretically, has recently been invoked to explain the weak suppression of  $T^*$  with  $x$ .<sup>14</sup>

In order to clarify the physical nature and origin of the anomalous stabilization of the correlated electron state in  $\text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5$ , we measured the pressure dependence of electrical resistivity  $\rho$  in single-crystal samples of  $\text{Ce}_{1-x}\text{R}_x\text{CoIn}_5$  with  $R = \text{Yb}, \text{Y}, \text{Gd}$ . Applied pressure generally increases the valence of Ce and Yb ions in metals by enhancing the hybridization strength between their  $f$  electrons and the conduction band, which “squeezes” an electron out of the  $4f$  shell and tends to drive Ce and Yb ions less and more magnetic, respectively. The effect of applied pressure on cooperative valence fluctuations in  $\text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5$  could manifest itself in contrasting behavior of the relevant energy scales as a function of pressure in samples containing intermediate-valent Yb ions when compared with samples with stable-valent Gd and Y ions. Our measurements indicate that the pressure dependence of  $T_c$  and  $T^*$  is similar for all samples, independent of the degree of valence stability of the rare-earth ion being introduced. This result may suggest that higher pressures are necessary to disrupt or perturb the cooperative intermediate-valence state of Ce and Yb ions in  $\text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5$ .

## II. EXPERIMENT

Single crystals of  $\text{Ce}_{1-x}\text{R}_x\text{CoIn}_5$  with  $R = \text{Yb}$  ( $x = 0.1, 0.2, 0.4$ ),  $\text{Y}$  ( $x = 0.2$ ), and  $\text{Gd}$  ( $x = 0.1$ ) were synthesized in a molten In flux using the same procedure reported elsewhere.<sup>6,8,15,16</sup> The samples were etched in a dilute HCl solution to remove residual In flux. Phase purity and chemical composition were verified by means of powder x-ray diffraction and energy-dispersive x-ray analysis, respectively. Measurements of electrical resistivity  $\rho$  under applied pressure were performed up to 25 kbar in a clamped piston cylinder pressure cell and down to  $\sim 1.1$  K in a pumped  $^4\text{He}$  Dewar. A 50:50 mixture of  $n$ -pentane and isoamyl alcohol was used to provide a hydrostatic pressure transmitting medium. Annealed Pt leads were affixed to gold-sputtered contact surfaces on each sample with silver epoxy in a standard four-wire configuration. The pressure dependence of the SC  $T_c$  of high-purity Sn, measured inductively, was used as a manometer by calibrating against data from Ref. 17.

## III. RESULTS AND DISCUSSION

Representative  $\rho$  vs  $T$  data between  $\sim 1.1$  and 300 K are displayed in Fig. 1(a) for  $\text{Ce}_{0.9}\text{Yb}_{0.1}\text{CoIn}_5$ . The salient details exhibited by  $\rho(T)$  primarily include a maximum at  $T^*$  and superconductivity below  $T_c$ . The maxima in  $\rho$  at  $T^*$ , which are emphasized in the inset of Fig. 1(a) at several applied pressures, are generally interpreted as indicating the onset of coherent scattering in a Kondo lattice.<sup>6,8</sup>  $T^*$  increases with applied pressure, which agrees with previously reported results from measurements of  $\text{CeCoIn}_5$ .<sup>18</sup>  $\rho$  data in the vicinity of  $T_c$

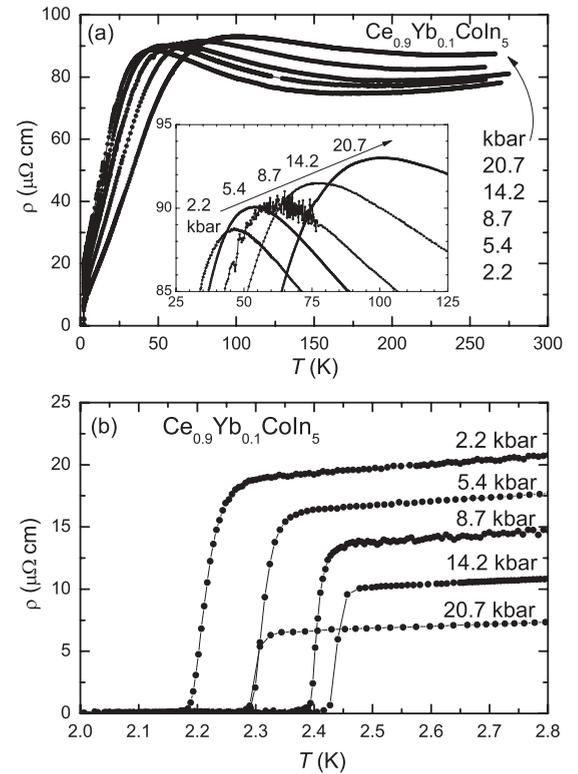


FIG. 1. (a) Representative  $\rho$  vs  $T$  data for  $\text{Ce}_{0.9}\text{Yb}_{0.1}\text{CoIn}_5$  measured under applied quasihydrostatic pressures of 2.2, 5.4, 8.7, 14.2, and 20.7 kbar. The inset focuses on the region around maxima in  $\rho(T)$  at  $T^*$ .  $T^*$  increases with applied pressure. Lines are guides to the eye. (b)  $\rho$  vs  $T$  for  $\text{Ce}_{0.9}\text{Yb}_{0.1}\text{CoIn}_5$  at low temperature, emphasizing the sharp transitions into the SC state at  $T_c$ . Lines are guides to the eye.

are displayed in Fig. 1(b) where sharp resistive drops, which are consistent with high-quality samples with good chemical homogeneity, are observed. Nicklas *et al.* previously reported that the resistive transition width  $\Delta T_c$  in  $\text{CeCoIn}_5$  decreased (sharpened) from 80 mK at ambient pressure to 20 mK for  $P > 0.9$  GPa.<sup>18</sup>  $\Delta T_c$  for  $\text{Ce}_{0.9}\text{Yb}_{0.1}\text{CoIn}_5$  decreases monotonically from 113 mK at ambient pressure to 52 mK at 20 kbar as seen in Fig. 1(b), which is in qualitative agreement with the results for  $\text{CeCoIn}_5$ .<sup>18</sup> If we extrapolate the normal-state  $\rho$  to zero temperature using the local slope  $d\rho/dT$  just above  $T_c$ , we are able to estimate the residual resistivity  $\rho_0$ , which decreases with increasing pressure. This is also consistent with the behavior previously reported for  $\text{CeCoIn}_5$ .<sup>18</sup>  $\rho(T)$  data for samples other than  $\text{Ce}_{0.9}\text{Yb}_{0.1}\text{CoIn}_5$  which were measured are not shown herein, but their quality and character are commensurate with those displayed in Figs. 1(a) and 1(b).

Data for  $T_c$  vs  $P$  for all samples measured as part of this study are shown in Fig. 2 in addition to data for  $\text{CeCoIn}_5$  taken from Ref. 18. The values for  $T_c$  were determined from the midpoint of each sharp resistive transition. SC domes, such as those seen in Fig. 2, are commonly observed in materials with a nearby QCP which exhibit unconventional SC states wherein Cooper pairing is mediated by QC spin fluctuations.<sup>5</sup> A specific theory for a  $d$ -wave SC state in close proximity to an antiferromagnetic instability<sup>19,20</sup> has previously been invoked to study and describe  $T_c(P)$  for  $\text{CeCoIn}_5$ .<sup>18</sup> Without appealing

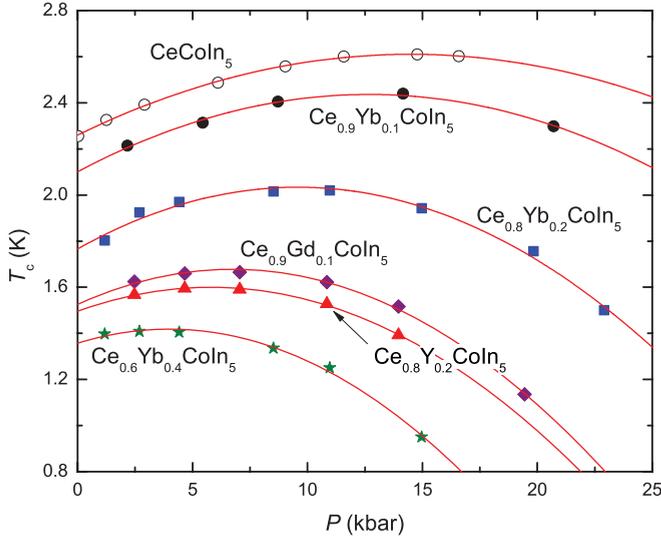


FIG. 2. (Color online) SC  $T_c$  vs  $P$  for all samples measured in this study in addition to data for  $\text{CeCoIn}_5$  from Ref. 18. The general character of the SC domes appears to be qualitatively similar for each sample, independent of the identity of the rare-earth ion being introduced or its concentration. The red lines are nonlinear least-squares fits of Eq. (1) to the data.

to any particular theory, we observe that a simple expression

$$T_c = T_{\max} + \lambda(P - P_{\max})^2 \quad (1)$$

is naturally suggested by the character of the data shown in Fig. 2, where the maximum  $T_c$  in each dome is denoted  $T_{\max}$ , the pressure at which  $T_{\max}$  occurs is  $P_{\max}$ , and  $\lambda$  characterizes the amplitude of parabolic curvature of the dome. The results of nonlinear least-squares fits of Eq. (1) to  $T_c(P)$  data are shown in Fig. 2 as red lines. The close agreement between fits and data for all samples indicates that Eq. (1) with its three parameters adequately describes the character of these SC domes. A systematic relationship between best-fit values for fit parameters and a sample-dependent characteristic is most clearly illustrated in Figs. 3(a)–3(c) by plotting  $T_{\max}$ ,  $P_{\max}$ , and  $\lambda$  values, respectively, as a function of  $T_c(0)$  for each sample. These plots demonstrate that each parameter is a linear function of  $T_c(0)$  for all samples studied, irrespective of rare-earth ion  $R$  identity or concentration  $x$ . As a consequence, the character of  $T_c(P)$  is primarily determined by  $T_c(0)$ . This result suggests that two samples with appropriately selected concentrations of Yb and Y, for example, such that each has identical  $T_c(0)$ , will exhibit indistinguishable SC domes  $T_c(P)$ .

The pressure dependence of  $T^*$  for each sample is shown in Fig. 4 alongside data for  $\text{CeCoIn}_5$  taken from Ref. 18. We defined  $T^*$  by determining the temperature of maxima in  $\rho(T)$  [where  $d\rho(T)/dT = 0$ ] such as those shown in Figs. 1(a) and 1(b). Conventional wisdom dictates that the application of pressure tends to increase the Kondo-lattice coherence temperature in Ce-based Kondo systems.  $T^*$  increases with pressure with roughly the same  $\sim 2.8 \text{ K kbar}^{-1}$  slope which was previously reported for  $\text{CeCoIn}_5$ .<sup>18</sup> It appears that the character of  $T^*$  can be described by  $T^*(P) = T^*(0) + \xi P$ , where  $\xi \equiv dT^*/dP$  is apparently independent of the details of

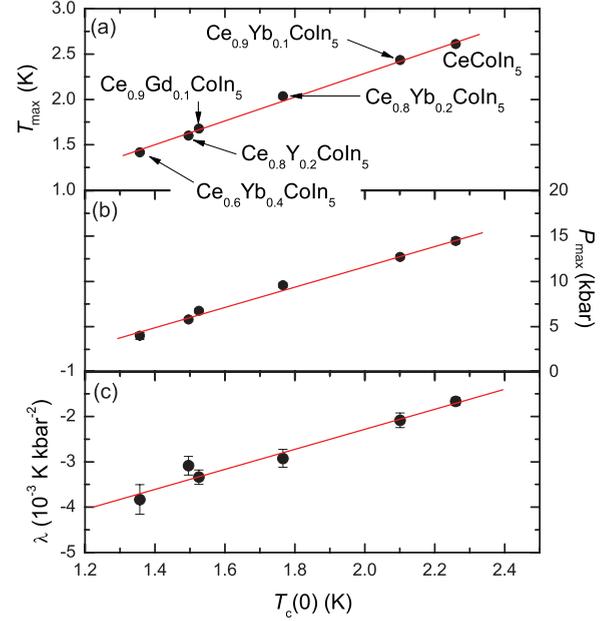


FIG. 3. (Color online) Best-fit values of parameters from fits of Eq. (1) to  $T_c(P)$  data for (a)  $T_{\max}$ , (b)  $P_{\max}$ , and (c)  $\lambda$  parameters plotted vs  $T_c(0)$ . Each parameter appears to be a linear function of  $T_c(0)$ . Lines are guides to the eye.

$R$  and  $x$ . Only the ambient pressure parameter  $T^*(0)$  depends on those details, so the effect of pressure on the Kondo lattice in  $\text{Ce}_{1-x}R_x\text{CoIn}_5$  is universal up to  $\sim 25$  kbar, regardless of whether rare-earth ions with stable or unstable valences are substituted for Ce. Whatever novel mechanism stabilizes  $T^*$  for Yb substitution at ambient pressure<sup>6</sup> seems to be decoupled from the behavior of this system as a function of pressure; i.e., its character is insensitive to the nature and concentration of the Kondo holes in  $\text{CeCoIn}_5$ . In the context of the Kondo disorder model of Dzero and Huang,<sup>14</sup> this result suggests that correlations between Yb ions, the strength of which would

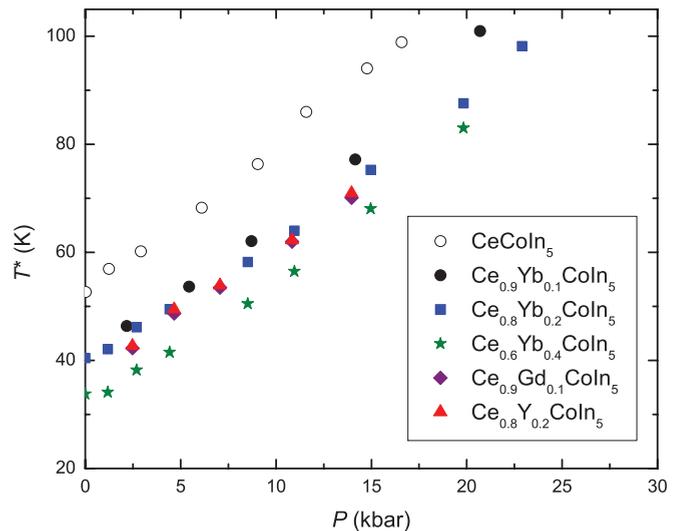


FIG. 4. (Color online)  $T^*$  increases linearly with  $P$  with a roughly universal slope for each sample measured as part of this study and in  $\text{CeCoIn}_5$  from Ref. 18.

presumably increase with pressure, might not play a major role. Although it was considered, we are currently unable to develop an interpretation of our results within the picture wherein interlaced networks of CeCoIn<sub>5</sub> and YbCoIn<sub>5</sub> coexist.<sup>13</sup>

#### IV. CONCLUSION

The behavior of the characteristic energy scales  $T_c(P)$  and  $T^*(P)$  in Ce<sub>1-x</sub>R<sub>x</sub>CoIn<sub>5</sub> ( $R = \text{Yb, Y, Gd}$ ) as a function of applied pressure appears to be determined by  $T_c(0)$  and  $T^*(0)$  alone. This insensitivity of the salient physics to the details of rare-earth ion  $R$  electronic configuration and concentration  $x$  is unexpected for two reasons: (1) at ambient pressure, the physical properties of Ce<sub>1-x</sub>Yb<sub>x</sub>CoIn<sub>5</sub> are significantly different<sup>6,7</sup> from those observed when other rare-earth ions are introduced,<sup>8</sup> and (2) it is possible, in principle, to perturb the electronic configuration of Yb by applying pressure, but not for rare-earth ions with stable valences such as Y and Gd. Our results imply that  $\sim 25$  kbar of applied pressure is insufficient to perturb the valence state of Yb ions. The pressure

dependencies of  $T_c$  and  $T^*$  are apparently governed by the increase in hybridization of local Ce  $4f$ - and conduction-electron states with pressure. It may, therefore, be instructive to study this system at higher pressures, focusing particularly on the behavior of  $T^*(P)$ . Such studies may more clearly elucidate the role that the Yb intermediate-valence state plays in Ce<sub>1-x</sub>Yb<sub>x</sub>CoIn<sub>5</sub>.

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\*Permanent address: Department of Physics, Fudan University, Shanghai 200438, People's Republic of China.

†Permanent address: Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

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