Resolution of the discrepancy between the variation of the physical properties of Ce$_{1-x}$Yb$_x$CoIn$_5$ single crystals and thin films with Yb composition

S. Jang$^{ab}$, B.D. White$^{bc}$, I.K. Lum$^{ab}$, H. Kim$^{de}$, M.A. Tanatar$^{de}$, W.E. Straszheim$^d$, R. Prozorov$^{de}$, T. Keiber$^f$, F. Bridges$^f$, L. Shu$^g$, R.E. Baumbach$^h$, M. Janoschek$^i$ & M.B. Maple$^{abc}$

$^a$ Materials Science and Engineering Program, University of California, La Jolla, San Diego, CA, 92093, USA.
$^b$ Center for Advanced Nanoscience, University of California, La Jolla, San Diego, CA, 92093, USA.
$^c$ Department of Physics, University of California, La Jolla, San Diego, CA, 92093, USA.
$^d$ Ames Laboratory, Ames, IA, 50011, USA.
$^e$ Department of Physics and Astronomy, Iowa State University, Ames, IA, 50011, USA.
$^f$ Physics Department, University of California, Santa Cruz, CA, 95064, USA.
$^g$ Department of Physics, Fudan University, Shanghai, 200433, People’s Republic of China.
$^h$ National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL, 32310, USA.
$^i$ Condensed Matter and Magnet Science, Los Alamos National Laboratory, Los Alamos, NM, 87545, USA.

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Resolution of the discrepancy between the variation of the physical properties of Ce$_{1-x}$Yb$_x$CoIn$_5$ single crystals and thin films with Yb composition

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$^a$Materials Science and Engineering Program, University of California, La Jolla, San Diego, CA 92093, USA; $^b$Center for Advanced Nanoscience, University of California, La Jolla, San Diego, CA 92093, USA; $^c$Department of Physics, University of California, La Jolla, San Diego, CA 92093, USA; $^d$Ames Laboratory, Ames, IA 50011, USA; $^e$Department of Physics and Astronomy, Iowa State University, Ames, IA 50011, USA; $^f$Physics Department, University of California, Santa Cruz, CA 95064, USA; $^g$Department of Physics, Fudan University, Shanghai 200433, People's Republic of China; $^h$National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310, USA; $^i$Condensed Matter and Magnet Science, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

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Extraordinary electronic phenomena including an Yb valence transition, a change in Fermi surface topology, and suppression of the heavy fermion quantum critical field at a nominal concentration $x \approx 0.2$ have been found in the Ce$_{1-x}$Yb$_x$CoIn$_5$ system. These phenomena have no discernable effect on the unconventional superconductivity and normal-state non-Fermi liquid behaviour that occur over a broad range of $x$ up to $\sim 0.8$. However, the variation of the coherence temperature $T^*$ and the superconducting critical temperature $T_c$ with nominal Yb concentration $x$ for bulk single crystals is much weaker than that of thin films. To determine whether differences in the actual Yb concentration of bulk single crystals and thin film samples might be responsible for these discrepancies, we employed Vegard’s law and the spectroscopically determined values of the valences of Ce and Yb as a function of $x$ to determine the actual composition $x_{\text{act}}$ of bulk single crystals. This analysis is supported by energy-dispersive X-ray spectroscopy, wavelength-dispersive X-ray spectroscopy, and transmission X-ray absorption edge spectroscopy measurements. The actual composition $x_{\text{act}}$ is found to be about one-third of the nominal concentration $x$ up to $x \sim 0.5$, and resolves the discrepancy between the variation of the physical properties of Ce$_{1-x}$Yb$_x$CoIn$_5$ single crystals and thin films with Yb concentration.

Keywords: chemical substitution; Vegard’s law; energy-dispersive X-ray spectroscopy; wavelength-dispersive X-ray spectroscopy; transmission X-ray absorption edge spectroscopy; intermediate valence; valence transition; unconventional superconductivity; Kondo lattice; heavy fermion behaviour

*Corresponding author. Email: mbmaple@ucsd.edu

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1. Introduction

The unusual effect of Yb substituents compared to that of other lanthanide substituents on the normal and superconducting state properties of the heavy fermion compound CeCoIn$_5$ has attracted much recent interest [1–11]. Measurements of the electrical resistivity $\rho(T)$, magnetic susceptibility $\chi(T)$, specific heat $C(T)$, and tetragonal $a$- and $c$-lattice parameters as a function of $x$, performed on flux-grown bulk single crystal specimens in independent studies by Capan et al. [1] and Shu et al. [2], yielded results that are in general agreement with one another. In the work of Shu et al. [2], the weak variations of the coherence temperature $T^*$ and superconducting critical temperature $T_c$ with Yb concentration $x$ were attributed to stabilization of the correlated electron state in the Ce$_{1-x}$Yb$_x$CoIn$_5$ system over a large range of $x$. Based on the strong deviation of the tetragonal $a$- and $c$-lattice parameters and unit cell volume $V = a^2c$ as a function of $x$ from Vegard’s law (linear variation of $a$- and $c$-lattice parameters with $x$) [12], it was suggested [2] that the stability of the correlated electron state in Ce$_{1-x}$Yb$_x$CoIn$_5$ could be due to cooperative behaviour of the Ce and Yb ions involving their unstable valences that can range from 3+ to 4+ in the case of Ce and 2+ to 3+ for Yb. Since the 4$f$-electron states of the Ce and Yb ions are admixed with conduction electron states, they communicate with one another through the conduction electrons. It was reasoned that the Ce and Yb ions could then self-consistently adjust their valences so as to stabilize the heavy electron state over a large range of Yb concentrations $x$. However, spectroscopic measurements (EXAFS, XANES, and ARPES) by Booth et al. [3] and Dudy et al. [8] found that the valence of Ce remains close to 3+ for $0 \leq x \leq 1$, whereas the valence of Yb remains close to 2.3+ for $0.2 \leq x \leq 1$. These results are not consistent with the aforementioned proposal [2] that the Ce and Yb valences vary with Yb concentration. It is noteworthy that the experiments of Dudy et al. [8] revealed that Yb undergoes a valence transition from 3+ at $x \approx 0$ to $\sim 2.3+$ at $x \approx 0.2$. While there are issues of phase separation at values of $x$ above $\sim 0.8$ [1,2], we emphasize that the valence of the pure YbCoIn$_5$ end-member compound ($x = 1$) was found to be $\sim 2.3+$ [3,8], which is important for the analysis presented herein.

Subsequent investigations of the Ce$_{1-x}$Yb$_x$CoIn$_5$ system revealed evidence for other electronic transitions at $x \sim 0.2$, including a reconstruction of the Fermi surface above $x \approx 0.2$, accompanied by a significant reduction in the quasiparticle effective mass [5], and suppression of the quantum critical field associated with the correlated heavy fermion state to 0 K at a quantum critical point at $x \approx 0.2$ [7,9]. Surprisingly, these transitions have little effect on the unconventional superconductivity and non-Fermi liquid (NFL) behaviour. Measurements of $T_c$ vs. $x$ in the range $x = 0$ and $x = 0.7$ show that $T_c$ decreases linearly with $x$ from 2.3 K at $x = 0$ and extrapolates to 0 K at $x \approx 1$, with no features near $x = 0.2$. The NFL signatures in $\rho(T)$, $C(T)$, and $\chi(T)$ persist from 0 to $x \approx 0.8$ with an abrupt crossover to Fermi liquid behaviour slightly above this value of $x$ [2,9]; this suggests that the NFL behaviour could be associated with a new state of matter rather than being a consequence of the underlying quantum phase transition at $x \approx 0.2$ and opens up the possibility that some other type of electronic transition occurs near $x \approx 0.8$ [13]. The region $0.8 \leq x \leq 1$ is currently being explored.

Measurements of electrical transport properties on Ce$_{1-x}$Yb$_x$CoIn$_5$ thin films revealed that the variation of the physical properties is much stronger than that observed in the Ce$_{1-x}$Yb$_x$CoIn$_5$ single crystals, but weaker than that which is found for other lanthanide substituents in CeCoIn$_5$ single crystals [6]; the rate of depression of $T^*$ and $T_c$ with
Yb concentration for the thin films is about three times greater than that observed in the single crystals. In this paper, we describe an analysis we have performed on bulk single crystals of Ce$_{1-x}$Yb$_x$CoIn$_5$ that apparently resolves the discrepancy between the bulk single crystal and thin film experiments. The analysis involves the application of Vegard’s law to estimate the actual composition $x_{\text{act}}$ using the variation of the tetragonal $a$- and $c$-lattice parameters and the spectroscopically determined valences of Ce and Yb as a function of nominal composition $x$ in flux-grown Ce$_{1-x}$Yb$_x$CoIn$_5$ single crystals. The analysis is unusual, since we are using the known valences of Ce and Yb as a function of $x$ to determine the actual Yb concentration $x_{\text{act}}$ (assuming that all of the lanthanide sites in the compounds are occupied by Ce or Yb ions; i.e. no lanthanide vacancies). In the usual Vegard’s law analysis, the lanthanide sites are occupied by lanthanide ions according to their nominal concentrations, and the deviations of the lattice parameters from Vegard’s law are used to estimate the valence of one of the lanthanide ions [14,15]. Direct support for the Vegard’s law analysis is provided by energy-dispersive X-ray spectroscopy (EDS), wavelength-dispersive X-ray spectroscopy (WDS), and transmission X-ray absorption edge spectroscopy (TXAS) measurements on selected single crystals, which are reported herein. Although XAS usually refers to both fluorescence and transmission data, only the step height in transmission data is proportional to the number of atoms within the X-ray beam and we use the designation TXAS to highlight this difference. The Vegard’s law analysis of the $a$- and $c$-lattice parameters indicates that the actual Yb composition of the single crystals is about one-third of the nominal composition in the range $0 \leq x \lesssim 0.5$, resolving the discrepancy between experiments on Ce$_{1-x}$Yb$_x$CoIn$_5$ single crystals and thin films. It is noteworthy that the actual composition of the Ce$_{1-x}$Yb$_x$CoIn$_5$ single crystals prepared from a molten indium flux is in registry with the nominal composition of the starting material contained in the molten flux, but is only about one-third of its value in the range $0 \leq x \lesssim 0.5$. The sharpness of the specific heat feature associated with the superconducting transition [1,2], which reflects the bulk behaviour of the crystals, indicates that the Ce$_{1-x}$Yb$_x$CoIn$_5$ single crystals are homogeneous up to Yb nominal compositions of $x \sim 0.5$. As a result, all of the experiments on Ce$_{1-x}$Yb$_x$CoIn$_5$ single crystals that have been performed in the range $0 \leq x \lesssim 0.5$ are still valid but the actual Yb concentration is about one-third of the nominal concentration; i.e. $x_{\text{act}} \approx x/3$. At higher $x$, the Vegard’s law analysis indicates that the ratio of $x_{\text{act}}$ to $x$ increases continuously with $x$ to the value of 1 at $x = 1$, as it must for the pure YbCoIn$_5$ end member compound.

In the study by Shu et al. [2], the samples selected for $\rho(T)$, $\chi(T)$, and $C(T)$ measurements had actual Yb compositions $x_{\text{act}}$, as determined from EDS measurements, that were close to the nominal composition $x$. We have performed further EDS measurements on samples with the same values of $x$ as those reported in the work of Shu et al. and found that the values of $x_{\text{act}}$, inferred from EDS measurements, exhibit bimodal behaviour in which $x_{\text{act}} \approx x/3$ for some crystals, whereas $x_{\text{act}} \approx x$ for other crystals, with large uncertainties in the values of $x_{\text{act}}$. A possible reason for this bimodal behaviour of $x_{\text{act}}$ may be that the single crystals have a bimodal Yb surface composition $x_{\text{act}} \approx x/3$ and $x_{\text{act}} \approx x$ and a bulk composition $x_{\text{act}} \approx x/3$. As we explain in the following, this result is consistent with an analysis based on the application of Vegard’s law to the unit cell volume, $V$, vs. $x$ data, where $V$ was determined from powder X-ray diffraction measurements of the tetragonal $a$- and $c$-lattice parameters (i.e. $V = a^2c$).
2. Experiment

Single crystals of Ce$_{1-x}$Yb$_x$CoIn$_5$ were grown using a molten indium flux method in alumina crucibles, as described previously [16]. Powder X-ray diffraction measurements, performed at room temperature, reveal that the Ce$_{1-x}$Yb$_x$CoIn$_5$ single crystals form in the tetragonal HoCoGa$_5$ structure. The tetragonal $a$- and $c$-lattice parameters were determined from a least squares fit of the peak positions in the X-ray powder diffraction pattern using GSAS and EXPGUI [17,18]. It should be noted that our lattice parameter values are in good agreement with those of Capan et al. [1]; however, in the analysis described below, we use the data for the $a$- and $c$-lattice parameters of Capan et al., since the scatter in their data is smaller than in ours.

EDS measurements were carried out at the University of California, San Diego on various samples that have been prepared for the experiments reported in Refs. [2,4,7–11], the WDS measurements were performed at Iowa State University, Ames National Laboratory, on samples studied in the penetration depth experiments and on several other samples with different Yb concentrations [10], while the TXAS measurements were performed at the Stanford Synchrotron Radiation Laboratory on samples specifically prepared for the TXAS measurements. The EDS, WDS, and TXAS measurements are discussed in more detail below.

Measurements of electrical resistivity were performed down to $\sim$1.1 K in a $^4$He Dewar using a Linear Research LR700 ac resistance bridge. Four wires were adhered to gold-sputtered contact pads on each single crystal using silver epoxy. Typical contact resistances of 100 m$\Omega$ or less were measured at room temperature by comparing two- and four-wire resistance measurements.

3. Results and discussion

Before determining the actual Yb concentration $x_{\text{act}}$ in single-crystalline samples of Ce$_{1-x}$Yb$_x$CoIn$_5$, we demonstrate that Yb is incorporated into the single crystals systematically and in registry with the nominal Yb concentration $x$. In Figure 1(a), the inverse of the residual resistivity ratio (RRR) is plotted vs $x$. We calculated the inverse of the RRR from electrical resistivity $\rho(T)$ measurements (not shown) on several single crystals as $\rho_0/\rho(300 \text{ K})$, where $\rho_0$ is the residual electrical resistivity. The data are plotted this way because $\rho_0/\rho(300 \text{ K})$ does not suffer from errors associated with measuring the geometrical factor. It is clear that the data in Figure 1(a) are linear up to $x = 0.5$, convincingly demonstrating that Yb is incorporated into the crystal structure systematically (i.e. temperature-independent impurity scattering characterized by $\rho_0$ increases relative to $\rho(300 \text{ K})$ with increasing nominal Yb concentration $x$). We are also able to demonstrate that the variation of the physical properties of the Ce$_{1-x}$Yb$_x$CoIn$_5$ system is a systematic function of the RRR as seen in the plot of superconducting critical temperature $T_c$ vs. RRR in Figure 1(b). This result further emphasizes that the RRR values meaningfully characterize the level of disorder in the single crystals, and that $x_{\text{act}}$ is in registry with $x$.

3.1. Estimate of actual Yb concentration using Vegard's law

Vegard’s law refers to the linear variation of the lattice parameters or unit cell volume when an element is substituted for another element in a compound for which the crystal
Figure 1. (a) Inverse of the RRR, calculated as $\rho_0/\rho(300\text{ K})$ from measurements of electrical resistivity on distinct samples, plotted vs. nominal Yb concentration $x$ for the Ce$_{1-x}$Yb$_x$CoIn$_5$ system. The dashed line is a guide to the eye. (b) Superconducting critical temperature $T_c$ plotted vs. RRR from the same measurements shown in panel (a). The dashed curve is a guide to the eye. Vertical bars characterize the width of the superconducting transitions and were calculated using the temperatures where $\rho(T)$ drops to 90 and 10% of its normal-state value just above $T_c$.

structure does not change and the chemical composition is known. This relation is often used to estimate the valence of lanthanide ions, which have valence instabilities such as Ce, whose valence can range from 3+ to 4+, and Sm, Eu, Tm, and Yb, whose valence can range from 2+ to 3+ [14,15]. In this work, we instead employ Vegard’s law in a different manner to estimate the actual Yb concentration $x_{\text{act}}$ in the Ce$_{1-x}$Yb$_x$CoIn$_5$ system using the valences of the Ce and Yb ions, derived from spectroscopic measurements, and the tetragonal $a$- and $c$-lattice parameters, determined from X-ray diffraction measurements on powdered Ce$_{1-x}$Yb$_x$CoIn$_5$ samples, as a function of nominal Yb concentration $x$. Since previous investigations have shown that the valence of Yb changes from 3+ to 2.3+ for all concentrations greater than $x = 0.2$ [3,8], the unit cell volume $V = a^2 c$ of Ce$_{1-x}$Yb$_x$CoIn$_5$ should be a linear function of $x$ between 0.2 and 1.0, according to Vegard’s law. We would expect a subtle non-linear variation of $V$ with $x$ for $x < 0.2$ as the Yb valence changes from 3+ to 2.3+ in the range $0 < x \leq 0.2$. In Figure 2, we show a plot of the measured unit cell volume $V$ vs. $x$, based on the X-ray
diffraction measurements of $a$ and $c$-lattice constants for Ce$_{1-x}$Yb$_x$CoIn$_5$ as a function of $x$, and a plot of $V$ vs. $x$ based on Vegard’s law. The lattice parameter data of Capan et al. [1] were used since they show less scatter than the data of Shu et al. [2]. By adjusting the measured values of $V$ to the Vegard’s law curve (illustrated by the arrows in Figure 2), we can estimate the actual concentration $x_{\text{act}}$ of Yb. The values of $x_{\text{act}}$ determined by means of this procedure are shown in the $x_{\text{act}}$ vs. $x$ plot in Figure 3(b). For values of $x$ below $\sim 0.5$, the actual bulk Yb concentration $x_{\text{act}}$ is about one-third of the nominal concentration $x$. For comparison, Figure 3(a) shows $x_{\text{act}}$ vs. $x$ data based on EDS and PIXE measurements on flux grown Ce$_{1-x}$Yb$_x$CoIn$_5$ single crystals prepared at UC, Irvine and UC, San Diego. In Figure 3(a), the $x_{\text{act}}$ vs. $x$ data are consistent with $x_{\text{act}} \approx x/3$ for $x$ values up to $x \approx 0.6$. Shown in Figure 3(b) are measurements of the bulk concentration of Yb based on EDS, WDS, TXAS, described in the following, that are also seen to be consistent with $x_{\text{act}} \approx x/3$ up to $x \approx 0.5$.

3.2. EDS, WDS, and TXAS measurements of the actual Yb concentration

3.3. EDS measurements

The results of EDS measurements on selected Ce$_{1-x}$Yb$_x$CoIn$_5$ samples are shown in the $x_{\text{act}}$ vs. $x$ plot in Figure 3(b). The method in which the data were taken is illustrated in Figure 4, which shows photographs of several Ce$_{1-x}$Yb$_x$CoIn$_5$ samples with nominal Yb concentrations of $x = 0.175$ and 0.2, labelled with the letters A, B, C, and D, that have been affixed to conducting carbon tape for the EDS measurements. The EDS measurements were
Figure 3. (colour online) (a) Actual Yb concentration $x_{\text{act}}$ vs. nominal Yb concentration $x$ as obtained from EDS measurements reported by Dudy et al. [8] (solid black squares) and PIXE and EDS measurements reported by Capan et al. [1] (solid red circles and solid inverted blue triangles, respectively). (b) Actual Yb concentration $x_{\text{act}}$ vs. nominal Yb concentration $x$ based on: (1) Vegard’s law analysis of $V(x)$ measurements (solid red triangles); (2) average value of the measured Yb concentration from several EDS measurements with error bars defined as the standard deviation (solid black circles); (3) WDS measurements (inverted unfilled triangles); (4) TXAS measurements (solid blue squares).

made on each of the samples at several different spots defined by the regions outlined by the black rectangles on the photographs of the crystals. The measured values of $x$, $x_{\text{meas}}$, for each of the regions are indicated in the lower panel of Figure 4(c) for the crystals labelled A, B, C, and D for the two selected Yb compositions, where the dashed lines indicate the average value of all the data for each Yb nominal concentration. The average values of the measurements and the error derived from the standard deviation are plotted as $x_{\text{act}}$ vs. $x$ in Figure 3(b).

3.4. WDS measurements

WDS measurements were performed using a JEOL JXA-8200 electron microprobe on all samples used in the London penetration depth study [10] and several representative
Figure 4. (colour online) Illustration of method for acquiring EDS data on the Ce$_{1-x}$Yb$_x$CoIn$_5$ single crystals. Multiple samples with $x = 0.175$ and 0.2 were affixed to conducting carbon tape for EDS measurements labelled with the letters A, B, C, and D. The EDS measurements were made on each sample within several different regions with varying sizes enclosed by the black rectangles. The results of the measurements are plotted as the red and black solid circles for $x = 0.175$ and 0.2, respectively. The dashed lines represent the average value of the data and are denoted as $x_{\text{act}}$ in Figure 3 for each of the two concentrations.

samples at other nominal concentrations of Yb, including samples with Yb from different sources. The composition of each single crystal was measured at 12 different locations on typically 0.5 × 0.5 mm$^2$ samples and averaged, yielding a statistical error of compositional measurement of about $\Delta x = \pm 0.005$. This error bar is substantially smaller than that of the EDS measurements because of the weakness of the Yb line, which causes the EDS measurements to have significantly lower spectral resolution and a small signal-to-noise ratio. The M-lines of Yb as measured in materials with Yb$^{3+}$, YbF$_3$ and YbRh$_2$Si$_2$ are shown in Figure 5(a) and (b) for data normalized at the peak position. The data for YbCoIn$_5$ and Ce$_{1-x}$Yb$_x$CoIn$_5$ with a nominal Yb concentration of $x = 0.40$ are also shown in Figure 5(a) and (b). Two features in the data should be noted. First, the M-lines in compounds with Yb$^{3+}$ are slightly shifted with respect to the lines in both YbCoIn$_5$ and Ce$_{1-x}$Yb$_x$CoIn$_5$, where the lines coincide. These observations are consistent with an Yb valence that is different from 3+ in Ce$_{1-x}$Yb$_x$CoIn$_5$ compounds for the whole series and are in agreement with previous spectroscopic measurements of the Yb valence [3,8]. This result provides direct evidence that Yb substitution induces hole doping, similar to Cd substitution [19]. Furthermore, both direct comparison of the spectra in Figure 5(a) and more quantitative analysis of $x$, taking into account mutual absorption, show that the actual Yb concentration $x_{\text{act}}$ is proportional to and smaller in magnitude than the nominal Yb concentration $x$, roughly by a factor of 3, as shown in Figure 3.
Figure 5. (colour online) Results of WDS measurements performed on samples used in a penetration depth study [10] for two representative samples with nominal Yb concentrations $x = 0.4$ and $x = 1$ and two compounds in which Yb is trivalent, YbF$_3$ and YbRh$_2$Si$_2$. (a) M-line of Yb for the four compounds. (b) Data in Figure 5(a) normalized at the peak position. Note that the M-lines in the compounds with Yb$^{3+}$ are slightly shifted with respect to the lines in both YbCoIn$_5$ and Ce$_{1-x}$Yb$_x$CoIn$_5$, where the lines coincide. These observations are consistent with an Yb intermediate valence of 2.3+ for Ce$_{1-x}$Yb$_x$CoIn$_5$ in the range $0.2 \leq x \leq 1$.

Figure 6. (colour online) Plots of the Co K (a) and Yb L$_{III}$ (b) edges after a linear pre-edge subtraction, which sets the pre-edge region at zero. A straight line fit above the edge shown as a black line provides an estimate of the step height at the edge. The data just above each edge that contain the XANES structure were not included in this straight line fit.
3.5. **TXAS measurements**

To determine the Ce and Yb concentrations relative to Co from X-ray absorption spectroscopy, the absorption step heights at the Ce and Yb L_{III} edges and the Co K edge were measured in transmission. The advantage of transmission measurements is that they do not just detect the atoms near the surface of the material, but instead probe all the atoms of interest, since the X-ray beam passes through the sample. The drawback is that they also detect atoms associated with inclusions that consist of the flux (in this case, indium) or impurity phases. For each thin powdered sample, transmission data were collected at the same point on the sample. The transmission step height is a direct measure of the number of atoms in the beam; using thin layers minimizes the effects of sample pinholes and inclusions. We have also checked that using a thicker sample (twice as thick) gives the same step-height ratios. Examples at the Yb L_{III} and Co K-edge are shown in Figure 6.

To obtain the atomic ratios, we first normalize each step by the known absorption step per atom for that element, from the MacMaster X-ray absorption cross-sections [20]; then the atomic ratios are given by the ratios of these normalized step heights. Assuming the Co site is fully occupied, this ratio directly gives the Yb or Ce concentration. The errors in such concentration measurements are about 5%. A similar approach was used to determine the Zn concentration in Zn-doped LiNbO_{3} [21]. The measured Ce concentrations are close to the nominal values, but the Yb concentrations are much lower than expected. The Yb concentrations are plotted in Figure 3(b), which shows $x_{\text{act}}$ vs. $x$, for two samples with nominal Yb concentrations of 0.3 and 0.4.
Figure 8. (colour online) Coherence temperature $T^*$ and superconducting critical temperature $T_c$ vs. actual Yb composition, $x_{\text{act}}$, for flux grown single crystals [2] and thin films [6]. The actual Yb concentration $x_{\text{act}}$ for the single crystals was inferred from the nominal concentration as described in the text, while $x_{\text{act}}$ for the thin films is the same as the nominal Yb composition.

3.6. Correction of the $T$ vs. Yb concentration phase diagram

The values of the actual Yb concentration, $x_{\text{act}}$, determined from the Vegard’s law procedure and supported by the measurements of $x_{\text{act}}$ described above, can now be used to correct the $T$ vs. Yb concentration phase diagram proposed in Refs. [1,2]. In Figure 7, the values of the superconducting critical temperature $T_c$ are shown vs. the actual concentration $x_{\text{act}}$, and compared to the data for the studies on thin films by Shimozawa et al. [6]. The $T_c$ vs. $x_{\text{act}}$ phase boundary for both the bulk single crystal and thin film measurements are in good agreement with one another, which supports the procedure to determine the actual Yb concentration we have employed in this work. A revised phase diagram that includes the $T_c$ vs. $x_{\text{act}}$ phase boundary and the dependence of the Kondo lattice coherence temperature $T^*$ on $x_{\text{act}}$ is displayed in Figure 8. The only remaining discrepancy between the behaviour of bulk single crystals and thin film samples is that, while $T^*$ is monotonically suppressed in the thin film samples with increasing $x_{\text{act}}$, $T^*$ increases with increasing $x_{\text{act}}$ above $x_{\text{act}} \sim 0.25$ in single crystals. While we do not understand the origin of this discrepancy, we note that the thin film samples differ from the single crystals through the presence of the substrate, arrested $a$-lattice parameter, etc. [6].

This revision of the phase diagram of Ce$_{1-x}$Yb$_x$CoIn$_5$ does not change any of the interesting physics that has been found for this extraordinary system, but simply readjusts the concentration at which various phenomena occur. In particular, we now conclude that the valence transition of Yb from 3.0+ to 2.3+ occurs between $x = 0$ and $\sim 0.07$.

4. Concluding remarks

The analysis involving Vegard’s law and the spectroscopically determined valences of Ce and Yb as a function of the nominal concentration $x$ in the Ce$_{1-x}$Yb$_x$CoIn$_5$ system have yielded estimates of the actual Yb concentration $x_{\text{act}} \approx x/3$ for $x$ below $\sim 0.5$. The relation between $x_{\text{act}}$ and $x$ derived from this analysis is supported by the results of EDS, WDS, and TXAS measurements reported in this work. The subnominal Yb concentration
encountered in the flux grown \( \text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5 \) single crystals is not without precedent for other substituents in CeCoIn\(_5\). For instance, Cd, Hg, and Sn substitution on the indium site occurs at fractional values of the nominal concentration [19,22,23]. In addition, there is a strong preference for substitution on the In(1) site [24], which has implications for how the electronic structure is tuned. Similar obstacles are also seen for Pt and Ru substitution [23,25]. Moreover, in the case of \( \text{CeCo}_{1-x}\text{Ru}_x\text{In}_5 \), not only is the measured \( x \) less than the target \( x \), but it is also seen that the Ru ions form clusters in the 115 lattice (at least on the surface of the flux grown crystals) [25]. There is evidence that such problems may also be found in other transition metal substitution series: e.g. the broad region of coexistence of antiferromagnetism and superconductivity in the \( T-x \) phase diagram for \( \text{CeCo}_{1-x}\text{Rh}_x\text{In}_5 \) may suggest phase separation in localized regions of individual crystals [26]. An exception to these difficulties is seen for lanthanide substitution of the Ce site (e.g. in \( \text{Ce}_{1-x}\text{R}_x\text{CoIn}_5 \) \( (\text{R} = \text{Y}, \text{La}, \text{Pr}, \text{Nd}, \text{Gd}, \text{Dy}, \text{Er}, \text{and Lu}) \)), which appears to be straightforward [27–29]. However, as we have described above, \( R = \text{Yb} \) substitution is problematic and occurs only at fractional values of the nominal concentration, similar to what is seen for substitution on the indium and transition sites. This result accounts for our earlier reports of an exceptional \( T-x \) phase diagram for \( \text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5 \) and, upon rescaling of \( x \), our phase diagram is now in close agreement with that of thin films of \( \text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5 \). Notably, it is important and interesting that the actual concentration \( x_{\text{act}} \) is in registry with the nominal concentration \( x \) of the starting material in the molten In flux. As a result, none of the interesting physics that has been found for this extraordinary system is changed; the various electronic transitions and phenomena simply occur at an actual Yb concentration \( x_{\text{act}} \approx x/3 \) for \( x \) below \( \sim 0.5 \). In particular, we now conclude that the valence transition of Yb from 3.0+ to 2.3+ occurs between \( x = 0 \) and \( \sim 0.07 \). As we noted above, Vegard’s law is ordinarily used to determine changes of valence of lanthanide ions with unstable valence when the lanthanide sites are completely occupied by lanthanide ions. In the present case, we use the known valences of the Ce and Yb ions as a function of \( x \), determined from spectroscopy, and Vegard’s law to estimate the actual concentration \( x_{\text{act}} \) of the Yb ions. This resolves the discrepancy between the variation of the coherence temperature \( T^* \) and the superconducting critical temperature \( T_c \) with Yb substituent concentration in the \( \text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5 \) bulk single crystals and thin films.

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**References**


