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Tuning the magnetic ground state of $\text{Ce}_{1-x}\text{Yb}_x\text{RhIn}_5$ by Yb valence fluctuations


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We characterize the properties of $\text{Ce}_{1-x}\text{Yb}_x\text{RhIn}_5$ single crystals with $0 \leq x \leq 1$ using measurements of powder x-ray diffraction, energy dispersive x-ray spectroscopy, electrical resistivity, magnetic susceptibility, specific heat, x-ray absorption near edge structure (XANES), and neutron diffraction. The Yb valence $v_{\text{Yb}}$ calculated from the magnetic susceptibility and measured using XANES, decreases from 3 at $x = 0$ to ~2.1 at $x_{\text{act}} = 0.2$, where $x_{\text{act}}$ is the measured Yb concentration. A transition from incommensurate to commensurate antiferromagnetism is observed in neutron diffraction measurements along $Q = (0.5, 0.5, 1)$ between 0.2 $\leq x_{\text{act}} \leq 0.27$; this narrative is supported by specific-heat measurements in which a second robust feature appears at a temperature $T_1 (T_c < T_1)$ for the same concentration range. Magnetic susceptibility measurements also reveal features which provide additional evidence of magnetic ordering. The results of this study suggest that the evolution of the Yb valence plays a critical role in tuning the magnetic ground state of $\text{Ce}_{1-x}\text{Yb}_x\text{RhIn}_5$.

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I. INTRODUCTION

Numerous studies on Ce-based heavy-fermion compounds, notably the $\text{CeMIn}_5$ ($\text{M} = \text{Co, Rh, Ir}$) family of compounds, have demonstrated the crucial role played by $4f$ electrons in unconventional superconductivity (SC), magnetic order, quantum criticality, and valence fluctuations [1–4]. The compound $\text{CeRhIn}_5$ is an ideal system in which to study the coexistence between magnetism and SC. Its temperature-pressure ($T$-$P$) phase diagram shows antiferromagnetic (AFM) ordering below a Néel temperature $T_N = 3.8 \text{ K}$ at ambient pressure, with $T_N$ being suppressed to a quantum critical point as pressure is applied at a critical pressure $P_c = 2.25 \text{ GPa}$. Near $P_c$, a broad dome of unconventional superconductivity with a maximum superconducting critical temperature of $T_c = 2.2 \text{ K}$ is found. The compound $\text{CeRhIn}_5$ is a relatively rare case in which the characteristic temperatures $T_N$ and $T_c$ are of the same magnitude, indicating a robust competition between antiferromagnetism and superconductivity [5–9].

Neutron diffraction experiments on $\text{CeRhIn}_5$ in zero applied magnetic field revealed that the antiferromagnetic ground state consists of antiferromagnetically coupled spin spirals that propagate along the $c$ axis as characterized by propagation vector $q_M = (0.5, 0.5, 0.297)$ in terms of the reciprocal lattice units $2\pi/a, 2\pi/b, 2\pi/c$ (r.l.u.) and with Ce ion magnetic moments that reside within the tetragonal basal plane [6,10]. Neutron spectroscopy further demonstrated that this complex spiral ground state is a consequence of frustrated nearest- and next-nearest-neighbor exchange interactions along the $c$ axis [11]. A spin-flop transition is observed when an external magnetic field of $\mu_0 H = 2 \text{ T}$ is applied within the $ab$ plane [6,12]. Here, the magnetic field induces a surprisingly large easy-axis magnetic anisotropy that together with frustrated exchange interactions results in a rich low magnetic field phase diagram that can be explained by a model related to the axial next-nearest-neighbor Ising (ANNNI) model [13]. At low temperatures $T < T_1$ the field-induced easy-axis anisotropy results in a commensurate, “++−−” magnetic structure, where the magnetic moments lying in the $ab$ plane follow an up-up-down-down periodicity along the $c$ axis [6,13]. A third, incommensurate magnetic phase is observed in the region $T_1 < T < T_N$, where the effect of the anisotropy is softened due to magnetic fluctuations arising near $T_N$. This results in an elliptical spin spiral with modulated magnetic moments that are predominantly oriented along the easy axis but exhibit small components perpendicular to it [6].

In agreement with the ANNNI model the propagation vector of the elliptical phase is strongly temperature dependent [13]. A study at higher magnetic fields uncovered evidence for nematic ordering similar to what is observed in iron-based...
superconductors [14]. These recent studies suggest that the magnetic order in CeRhIn$_5$ is highly tunable and here we explore this in more detail by means of Yb substitution on the Ce site.

The striking effects of Yb substitution on the physical properties of the heavy-fermion superconductor CeCoIn$_5$, which have been reported in detail [15–19], motivated us to study the related system Ce$_{1-x}$Yb$_x$RhIn$_5$. One interesting materials science issue encountered in the Ce$_{1-x}$Yb$_x$CoIn$_5$ system is the discrepancy between the nominal Yb concentration $x_{\text{nom}}$ and the actual Yb concentration $x_{\text{act}}$ of the flux-grown single crystals; this issue is discussed in Refs. [20,21]. While the Ce valence remains stable at $x=0$ for all $x$ in the Ce$_{1-x}$Yb$_x$CoIn$_5$ system, the Yb valence decreases from $x=0$ to $2.3+1$ near $x_{\text{nom}}=0.2$ [22]. At the critical concentration of $x_{\text{nom}}=0.2$ where the Yb valence stabilizes, various unusual phenomena emerge. At this Yb concentration, the Fermi surface undergoes a reconstruction [23] and the quantum critical field $H_{\text{QC}}$ is suppressed [24]. There is also evidence from London penetration depth measurements that the nodal superconducting energy gap of CeCoIn$_5$ crosses over to a nodeless gap at this Yb concentration [25]; on the other hand, recent thermal conductivity measurements are consistent with a robust nodal superconducting energy gap for all Yb concentrations [26]. Identifying the symmetry of the superconducting order parameter remains an interesting and unresolved issue in the system Ce$_{1-x}$Yb$_x$CoIn$_5$.

In this paper, we report the results of powder x-ray diffraction (XRD), energy dispersive x-ray spectroscopy (EDS), electrical resistivity, magnetization, specific heat, and neutron scattering measurements on the Ce$_{1-x}$Yb$_x$RhIn$_5$ system; these measurements reveal many similarities with the Ce$_{1-x}$Yb$_x$CoIn$_5$ system. The unit-cell volume vs $x$ exhibits an analogous deviation from Vegard’s law, demonstrating a discrepancy between Yb concentrations $x_{\text{act}}$ and $x_{\text{nom}}$. The Yb valence, which is determined through multiple experimental techniques, is found to change from 3+ to 2.1+ near $x_{\text{act}}\approx 0.2$. Neutron diffraction measurements show that there is also a crossover from an incommensurate to a commensurate magnetic structure near this Yb concentration. Furthermore, a second feature, presumably of magnetic origin, emerges in specific-heat measurements for samples with $x_{\text{act}}\geq 0.18$. These and other observations hint at a potential relationship between the magnetic ground state in Ce$_{1-x}$Yb$_x$RhIn$_5$ and the valence of Yb. Since the discrepancy in Yb concentration of Ce$_{1-x}$Yb$_x$RhIn$_5$ single crystals is qualitatively identical to that of Ce$_{1-x}$Yb$_x$CoIn$_5$ and thoroughly explained in the paper of Jang et al. [21], all of the references to Yb concentration $x$ in this paper represent the actual Yb concentration ($x=x_{\text{act}}$).

II. EXPERIMENTAL DETAILS

Single-crystalline samples of Ce$_{1-x}$Yb$_x$RhIn$_5$ were grown using a molten indium flux method [27]. For concentrations $x_{\text{nom}} > 0.9$, heat treatment at significantly higher temperature ($T > 1300^\circ\text{C}$) is required with the elements sealed in a metallic crucible, such as a Ta or Mo tube, as opposed to quartz in order to successfully grow the crystals [28]. Since our laboratory did not have access to these temperatures or metallic crucibles, we attempted to grow these Yb-rich compounds with $T < 1200^\circ\text{C}$ in a quartz crucible. This resulted in an inability to form high-quality single crystals with $0.28 \leq x_{\text{act}} \leq 1$. Additionally, the reported discrepancies in the Yb concentration could be attributed to this difficulty in synthesizing crystals with higher Yb concentrations due to the lower than ideal melting temperatures in conjunction with the potential for the Yb to react with the excess In to form the binary compound YbIn$_3$. For these reasons, we were unable to perform reliable measurements, including neutron scattering, on single crystals of Ce$_{1-x}$Yb$_x$RhIn$_5$ for $0.28 \leq x_{\text{act}} \leq 1$. Polycrystalline ingots of Ce$_{1-x}$Yb$_x$RhIn$_5$ were formed using traditional arc-melting techniques for selected Yb concentrations. X-ray diffraction (XRD) measurements were performed on powdered single crystals in a Bruker D8 Discover x-ray powder diffractometer using a Cu-$K_\alpha$ source to characterize the crystal structure. Analysis of chemical compositions was performed through transmission x-ray spectroscopy (TXAS) and energy dispersive x-ray spectroscopy (EDS) measurements, as described previously [21].

Magnetic susceptibility measurements were performed between 300 and 2 K using a magnetic property measurement system (MPMS) equipped with a 7-T superconducting magnet from quantum design (QD). Four-wire electrical resistivity measurements were performed from 300 K down to 1.1 K in a pumped $^4$He Dewar. Specific-heat measurements were performed down to 1.8 K in a QD physical property measurement system (PPMS) DynaCool using a standard thermal relaxation technique. Extended x-ray absorption fine structure (EXAFS) measurements were collected on powdered samples at the SLAC National Accelerator Laboratory on beamline 4-1. Transmission spectroscopy measurements were performed on the Ce and Yb $L_{\text{III}}$ edges and on the Rh $K$ edge.

Neutron diffraction measurements were made on BT-4 and BT-7 triple-axis spectrometers at the NIST Center for Neutron Research (NCNR) [29]. Single crystals were mounted in the HHL scattering plane and measured with neutrons of incident energy $E_i=14.7$ meV ($\lambda = 2.359$ Å). Coarse collimations of open 80°-80°-120° or 40°-40°-40°-open full width at half-maximum (FWHM) were used on BT-7 and BT-4, respectively, while 10°-10°-40° and open-50°-40°-radial were used for the high-resolution diffraction with the position sensitive detector on BT-7. Measurements were performed either in a helium cryostat with a base temperature of 1.5 K, or a He$^3$ system with a base temperature of 0.3 K.

III. RESULTS AND DISCUSSION

A. X-ray diffraction

The crystal structure of Ce$_{1-x}$Yb$_x$RhIn$_5$ is tetragonal with space group $P4/mmm$ for all temperatures below 300 K and for all $x$ values. Rietveld refinements were performed on several XRD patterns using GSAS [30] and EXPGUI [31]. In Fig. 1, the powder XRD pattern for a representative sample is shown. The Rietveld refinement is plotted in red and the measured XRD data are plotted as a black curve. We obtained good agreement between the measured XRD pattern and the refinement calculations for the expected crystal structure, which is quantified by reduced $\chi^2$ values of less than 3 for most concentrations, but with some deviation when $x$ is large.
FIG. 1. A representative XRD pattern for the $x = 0.17$ sample is plotted. The expected Bragg peak positions are indicated with small ticks above the labeled 2θ axis. The calculated fit from Rietveld refinement is plotted as the top (red) curve and the deviation from the fit is shown as the bottom (black) curve above the Bragg peak indicators. The inset illustrates differences in the XRD patterns for different Yb concentrations over a narrow window of 2θ. The peaks shift slightly between $x = 0.03$ and 0.17, and then shift significantly for $x = 0.9$.

The inset of Fig. 1 illustrates the shift in Bragg-peak positions as $x$ increases, indicating systematic changes in the lattice parameters. Using the Rietveld refinement technique, lattice parameters $a$ and $c$ were determined and are plotted along with the calculated unit-cell volume in Fig. 2.

Single crystals of Ce$_{1-x}$Yb$_x$CoIn$_5$, synthesized using an indium flux technique, are well-known to have a sub-nominal Yb concentration. As part of this study, we found that our Ce$_{1-x}$Yb$_x$RhIn$_5$ single crystals also contain a subnominal Yb concentration. To address this issue in the Rh system, we used an indium flux technique, are well-known to have a sub-nominal Yb concentration. As part of this study, we found that our Ce$_{1-x}$Yb$_x$RhIn$_5$ single crystals also contain a subnominal Yb concentration. To address this issue in the Rh system, we used an indium flux technique, which was also used in our flux growth technique. With the relationship between $x_{\text{act}}$ and $x_{\text{nom}}$, ensuring that all subsequent discussions of Yb concentration can be limited to the actual concentration, such that $x = x_{\text{act}}$, unless otherwise stated.

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FIG. 2. (a) Unit-cell volumes, plotted as a function of $x_{\text{nom}}$, calculated from XRD and neutron diffraction measurements on single-crystal and polycrystalline samples. A linear extrapolation representing Vegard’s law between the two parent compounds is shown as a guide to the eye; the horizontal (black) arrow emphasizes the discrepancy between the measured behavior of $V(x)$ and the Vegard’s law construction. Plotted in the inset are the lattice parameters $a$ and $c$ vs $x_{\text{nom}}$. (b) Comparison between the nominal and actual Yb concentrations determined from EDS, TXAS, and XRD measurements. A dashed line is drawn with slope $x_{\text{act}} = x_{\text{nom}}/3$, which fits the single-crystal data well for concentrations $x_{\text{nom}} < 0.7$. For higher concentrations, the data deviate from this line and approach the $x_{\text{act}} = x_{\text{nom}}$ line. The results from EDS and XRD measurements on polycrystalline samples fit the expected relation shown by the line $x_{\text{act}} = x_{\text{nom}}$. Error bars where indicated represent one standard deviation throughout the paper. These analyses establish a relationship between $x_{\text{act}}$ and $x_{\text{nom}}$, ensuring that all subsequent discussions of Yb concentration can be limited to the actual concentration, such that $x = x_{\text{act}}$, unless otherwise stated.

B. XANES

The step height in the absorption edge in transmission x-ray spectroscopy (TXAS) is a direct measurement of the...
number of atoms in the unfocused x-ray beam. Consequently, the ratio of the edge step heights for different elements in a sample, keeping the illuminated region of the sample the same for each edge energy, provides a measure of the relative concentrations. To get actual concentration ratios, each edge step height must be divided by the absorption cross-sectional area for that element \[32\]. The absorption edge step height was obtained by subtracting the ratio of the edge step heights for different elements in a single sample, keeping the illuminated region of the sample the same for each concentration. This correction was included in \( p_{\text{Yb}^{2+}} \) and \( p_{\text{Yb}^{3+}} \) of the 2+ and 3+ valences, respectively. Then, the Yb average valence \( z \) is given by \( z = 2p_{\text{Yb}^{2+}} + 3p_{\text{Yb}^{3+}} \). These measurements show that the substituted Yb ion shifts from nearly trivalent \( \text{Yb}^{3+} \) at \( x = 0 \) down to intermediate-valence \( \text{Yb}^{2.1+} \) by \( x = 0.2 \).

FIG. 3. Un-normalized XANES data for Yb, Ce, and Rh. (a) Shows the Ce \( L_{\text{III}} \) XANES for \( \text{Ce}_{1-x}\text{Yb}_{x}\text{RhIn}_5 \) where \( x = 0.03 \) is the top black line, followed by \( x = 0.1 \) as the red intermediate line, and \( x = 0.17 \) as the lower blue line. (b) The Yb \( L_{\text{III}} \) XANES, and (c) the Rh \( K \) XANES are shown for the same concentrations. All data were collected at \( T = 200 \) K and the “pre-edge” has been subtracted from the data.

FIG. 4. Measured Yb \( L_{\text{III}} \) edge data for \( \text{Ce}_{1-x}\text{Yb}_{x}\text{RhIn}_5 \) are plotted as black circles. The fit to the two-edge model is shown as the red solid line, while the dashed green line represents the contribution from \( \text{Yb}^{2+} \), and the dashed blue line represents the contribution from \( \text{Yb}^{3+} \). The results are shown over the same energy ranges for \( x = 0.03, 0.1, \) and 0.17 in panels (a), (b), and (c), respectively.

FIG. 2(b) for Yb for comparison with EDS and XRD measurements.

The Ce \( L_{\text{III}} \) edge and Rh \( K \) edge exhibit only a single-edge feature which indicates that only one valence state is present for these elements in the material. In contrast, the Yb \( L_{\text{III}} \) edge, shown in detail in Fig. 4, is composed of two slightly offset edges, indicating a mixed valence state. We briefly describe the XANES analysis used to determine the valence states for the different concentrations. The \( \text{Yb}^{2+} \) and \( \text{Yb}^{3+} \) valence states have different edge energies which are offset by several eV. \( \text{Yb}^{2+} \) absorbs near \( 8938 \) eV and \( \text{Yb}^{3+} \) near \( 8946 \) eV. To quantitatively determine the valence, two different offset edges were fit to the XANES data. Each edge is a sum of a broadened step function plus a Gaussian peak, centered at the same energy; the edge step is modeled as a convolution of a Gaussian distribution with a unit step function, and all Gaussians are assumed to have the same width \( \sigma \). The relative amplitudes of the Gaussians, the locations of each edge \( E_1 \) and \( E_2 \), \( \sigma \), and relative step heights were all determined from nonlinear fits for each concentration. The fit was conducted only in the immediate vicinity of the edges where additional features of the XANES edge are minimal compared with the first, large peaks. In a recent XANES study of \( \text{CaF}_2: \text{Yb} \), the absorption matrix element for the \( 2+ \) valence was found to be about 7% lower than for the \( 3+ \) valence state \[33\]. This correction was included in estimating the fractions \( p_{\text{Yb}^{2+}} \) and \( p_{\text{Yb}^{3+}} \) of the \( 2+ \) and \( 3+ \) valences, respectively. The Yb average valence \( z \) is then given by \( z = 2p_{\text{Yb}^{2+}} + 3p_{\text{Yb}^{3+}} \). These measurements show that the substituted Yb ion shifts from nearly trivalent \( \text{Yb}^{3+} \) at \( x = 0 \) down to intermediate-valence \( \text{Yb}^{2.1+} \) by \( x = 0.2 \).
FIG. 5. Electrical resistivity data for selected samples of Ce$_{1-x}$Yb$_x$RhIn$_5$, normalized by electrical resistivity values measured at 200 K. The Kondo coherence feature for samples is observed near 25 K. (Inset) Example of $T^*$ being calculated for the $x = 0.2$ sample.

C. Electrical resistivity

Electrical resistivity measurements were performed on selected Ce$_{1-x}$Yb$_x$RhIn$_5$ samples. These data are plotted in Fig. 5 and show an evolution of the Kondo lattice with Yb concentration in the range 0 $\leq x \leq 0.27$. We observe a coherence peak associated with the Kondo lattice behavior which is manifested as a kneelike feature. In Fig. 6, the Kondo coherence temperature $T^*$ and $\rho(T^*)/\rho(200$ K) are plotted as a function of $x$. We defined $T^*$ as the temperature where the slope of the resistivity exhibits the largest change; an example of this procedure is provided in the inset of Fig. 5. Values for $T^*$ and $\rho(T^*)/\rho(200$ K) remain relatively stable with a slight dip as $x$ increases from 0 to 0.2, before being rapidly suppressed as the Kondo lattice loses coherence at higher values of $x$; this coincides with the concentration where the Yb valence stabilizes at $v_{Yb} = 2.1+$. The stability of the Kondo lattice in the region $x < 0.2$ may suggest a cooperative relationship between a decreasing, unstable Yb valence and the decrease in number of host Ce$^{3+}$ ions with increasing $x$. Once the Yb valence becomes stable at about 2.1+, the Kondo lattice behavior weakens as Ce is replaced by Yb. This $x$-dependent behavior of the Kondo lattice is consistent with other findings in the Ce$_{1-x}$Yb$_x$RhIn$_5$ system where the valence of Yb and the magnetic structure are intertwined.

For the samples whose measurements are presented in Figs. 5 and 6, the residual resistivity ratio (RRR) was calculated according to the relation

$$R_{RRR} = \frac{\rho(300 \text{ K})}{\rho(0 \text{ K})},$$

where the values of $\rho(0 \text{ K})$ were estimated by extrapolating the $\rho(T)$ data to 0 K. The RRR values for the nominal Yb concentration range 0 $\leq x_{\text{nom}} \leq 1$ are plotted in Fig. 7. The evolution of the RRR with $x_{\text{nom}}$ shows significantly large values of the RRR for both parent compounds ($x = 0$ and 1). However, as $x_{\text{nom}}$ is increased from 0, the RRR drops precipitously, which suggests a possible relationship between the RRR and the difficulty in synthesizing substituted samples of Ce$_{1-x}$Yb$_x$RhIn$_5$ (described in Sec. II).

D. Magnetic susceptibility

Measurements of magnetic susceptibility as a function of temperature were made with the magnetic field $H$ oriented both in the $ab$ plane and along the $c$ axis; the measured
data measured with magnetic field applied along the c-axis are not indicated with the dashed line. (b) Magnetic susceptibility data for Ce$_{1-x}$YbxRhIn$_5$ above the AFM transition but below the temperature range exhibiting Curie-Weiss behavior. The values of $\chi_{ab}/\chi_c$ at 10 K, which is the signature for the AFM transition, is indicated by a dotted black line that acts as a guide to the eye. The temperature of the maximum is denoted $TM$.

Two concentrations are highlighted in the inset of Fig. 8(a). The inflection point, which corresponds to a deviation from Curie-Weiss behavior and is consistent with the crystalline electric field effects observed in CeRhIn$_5$ [34,35]. The inset of Fig. 8(b) shows the ratio of magnetic susceptibility with magnetic field applied in both orientations at 10 K. The ratio is roughly constant at $\chi_{ab}/\chi_c = 0.5$ for $x < 0.3$.

The inverse of the magnetic susceptibility $\chi^{-1}$ vs $T$ is plotted over a large temperature range in Fig. 9(a). For all $x$, the $\chi(T)$ data can be described by the Curie-Weiss relation

$$M/H = C/(T - \Theta_{CW}),$$

where $C_0$ is the Curie constant and $\Theta_{CW}$ is the Curie-Weiss temperature. The average effective magnetic moment of the rare-earth ions, $\mu_{\text{eff}}$, is estimated using the relation $C_0 = \mu_{\text{eff}}^2 N_A/k_B$, where $N_A$ is Avogadro’s number and $k_B$ is Boltzmann’s constant.

Values of $\mu_{\text{eff}}(x)$ are found to decrease monotonically from $\sim 2.5 \mu_B$ for $x = 0$ to approximately $1.6 \mu_B$ at $x = 0.27$. To obtain an estimate for the valence of Yb, $v_{\text{Yb}}$, data for $\mu_{\text{eff}}(x)$ can be modeled using the equation

$$\mu_{\text{eff}} = \sqrt{(\mu_{\text{Ce}}^{3+})^2(1 - x) + (\mu_{\text{Yb}}^{3+})^2[v_{\text{Yb}}(x) - 2](x)},$$

where the free-ion values of $\mu_{\text{Ce}}^{3+}$ and $\mu_{\text{Yb}}^{3+}$ are 2.54 and 4.54 $\mu_B$, respectively, and $v_{\text{Yb}}$ represents the valence of Yb.

Values of $\mu_{\text{eff}}(x)$ are plotted in Fig. 9(b) as a function of $x$. The dashed lines represent the theoretical behavior for $\mu_{\text{eff}}(x)$ using Eq. (3) and assuming that all Yb ions are either divalent or trivalent. In these calculations, Ce is always assumed to be trivalent. We observe that $\mu_{\text{eff}}(x)$ follows the behavior...
expected for Yb\(^{3+}\) for very low \(x\) until it crosses over to being more consistent with Yb\(^{2+}\). This result is consistent with the study of Ce\(_{1-x}\)Yb\(_x\)CoIn\(_5\) where Yb is trivalent near \(x = 0\), but its valence decreases to an intermediate value of 2.3+ at \(x \approx 0.07\) \[22\]. We applied Eq. (3) to extract values for \(\nu_{Yb}\) as a function of \(x\); the values obtained are consistent with results from TXAS measurements as described in the discussion section.

E. Specific heat

Specific-heat measurements were performed in zero magnetic field on samples in the system Ce\(_{1-x}\)Yb\(_x\)RhIn\(_5\) with actual Yb concentrations of \(x_{\text{act}} = 0, 0.07, 0.13, 0.15, 0.17, 0.18, 0.2, 0.23,\) and 0.27. These data are displayed in Fig. 10(a) with \(C/T\) plotted as a function of temperature below 20 K. A dramatic evolution of the magnetic transition with Yb concentration is evident both in the suppression of \(T_N\) and in the change in magnitude of the feature at \(T_N\). These results are consistent with a similar evolution with \(x\) that was observed in the systems Ce\(_{1-x}\)La\(_x\)RhIn\(_5\) and Ce\(_{1-x}\)Y\(_x\)RhIn\(_5\) \[27,36\].

The magnitude of the peak at \(T_N\) decreases with increasing \(x\) as a broad hump feature emerges near \(T_N\). This broad hump is a signature of short-range magnetic correlations that take an increasing amount of the entropy, leaving a smaller peak feature with less entropy at \(T_N\) \[36\].

The Sommerfeld coefficient \(\gamma\) and Debye temperature \(\Theta_D\) were determined from these data by plotting \(C/T\) vs \(T^2\) and fitting the linear portion for \(T > T_N\) with the expression \(C/T \approx \gamma + \beta T^2\), where \(\beta = \frac{12 \pi^4 N \hbar^3}{5 \Theta_D^3}\). Such a procedure is shown for representative data in Fig. 10(b), where a linear region is seen for \(T > T_N\). The best-fit results for \(\gamma\) and \(\Theta_D\) are plotted as functions of \(x\) in Figs. 10(c) and 10(d), respectively. The Sommerfeld coefficient for most Yb concentrations is roughly \(\gamma \approx 200 \text{ mJ mol}^{-1} \text{ K}^{-2}\). \(\gamma\) was previously determined from low-temperature \((T < T_N)\) fits to \(C/T\) data in two studies of the system Ce\(_{1-x}\)La\(_x\)RhIn\(_5\) \[36,37\]; this procedure resulted in smaller values of \(\gamma\): \(<100 \text{ mJ mol}^{-1} \text{ K}^{-2}\) and \(<50 \text{ mJ mol}^{-1} \text{ K}^{-2}\) \[36,37\]. Kim et al. discussed the difficulty of extracting \(\gamma\) from data for CeRhIn\(_5\) because of the contributions due to magnetic order \[37\]. Our results for \(\gamma\) may be higher than previous results due to partial gapping of the Fermi surface that is associated with the formation of the spin density wave (SDW) ground state \[10\]. We extracted \(\gamma\) using data measured at \(T > T_N\) where the Fermi surface is presumably ungapped, while Refs. \[36,37\] used fits to data in the temperature range \(T < T_N\). The Debye temperature is relatively \(x\) independent, as expected, maintaining a value of \(\Theta_D \approx 200 \text{ K}\) for all Yb concentrations.

In zero magnetic field, the compound CeRhIn\(_5\) exhibits an incommensurate antiferromagnetic structure below \(T_N\), characterized by a wave vector \(q_M = (\frac{1}{4}, \frac{3}{4}, 0.297)\) and Ce moments that reside within the easy \(ab\) plane \[10\]. When a magnetic field is applied within the \(ab\) plane, a field-induced phase transition is observed \[6,12\]. Such a transition has also been observed in measurements on the system Ce\(_{1-x}\)La\(_x\)RhIn\(_5\) under similar conditions \[36\]. Below \(T_N\), as field is applied, CeRhIn\(_5\) enters the “++−−”, commensurate magnetic phase \[6\]. Data from heat-capacity measurements on CeRhIn\(_5\) in magnetic fields up to \(\mu_0 H = 9 \text{ T}\) are shown in Fig. 11(a). A magnetic-field-induced feature at \(T_I < T_N\) is observed when \(\mu_0 H \geq 3 \text{ T}\).
emergence of the incommensurate antiferromagnetic structure for $x_{\text{act}} = 0$ [11]. Another possibility is that changes in the Yb valence as $x$ is increased could affect the orbital characteristics of the $4f$ electronic wave function and, in turn, result in additional magnetic anisotropies that favor commensurate order. We note that such changes in orbital character have recently been reported both as a function of chemical substitution [38] and magnetic field [39]. Both $T_I$ and $T_N$ increase with increasing $H$, which is consistent with the $H$-$T$ phase diagram determined by Light et al. for the case of La substitution [36]. One possibility is for the two effects described above to work in tandem to generate the observed behavior. However, based on similarities to the Ce$_{1-x}$Yb$_x$CoIn$_5$ system, which exhibits a valence transition at the same value of $x$ where there is a change in the electronic structure, and the fact that the RRR is consistently large throughout the full range of $x$ shown in Fig. 7, it seems more likely that the latter mechanism involving changes in the orbital characteristics of the $4f$ electronic wave functions causes the modifications in the magnetic structure.

**F. Neutron diffraction**

Neutron diffraction measurements, collected in the $H$-$H$-$L$ scattering plane with neutrons of incident energy $E_i = 14.7$ meV, are able to probe the crystal structure, magnetic moments of the constituent ions, and the magnetic structure of the ordered ground states. We performed such measurements on our Ce$_{1-x}$Yb$_x$RhIn$_5$ single crystals to determine whether or not there is a link between the variation of the Yb valence and the magnetic structure. To extract meaningful magnetic moments from neutron scattering data, corrections for neutron-neutron absorption must be made [40]. Due to the large neutron absorption cross sections of both In and Rh, and the irregular shape of the samples, making the corrections is problematic in the present case and, hence, the moment values from the magnetic susceptibility measurements are likely more reliable.

An incommensurate AFM structure was found for samples with $x = 0.17$ and 0.2 that could be described by a propagation vector $q = (0.5, 0.5, 0.297(0.002))$; this magnetic structure is identical to that of CeRhIn$_5$ [10]. The magnetic scattering intensity is obtained in terms of absolute units by normalizing the integrated intensity of these magnetic reflections by the $(110)$ and $(002)$ nuclear reflections. Using the details of the magnetic structure determined by Bao et al. [41] for the parent compound, the results from neutron diffraction for Ce$_{1-x}$Yb$_x$RhIn$_5$ were expressed in units of $\mu_B^2$/f.u. and plotted as a function of temperature in Figs. 13(a)–13(c); the resulting intensities show the development of magnetic order as the temperature is cooled below the Néel temperature $T_N$.

A region of the $H$-$H$-$L$ zone in reciprocal space was mapped using the position-sensitive detector (PSD) for a representative concentration, $x = 0.17$; it is shown in Fig. 13(d). The PSD covers an angular range over five degrees in scattering angle, and hence data were collected for several scattering angles separated by $5^\circ$, rotating the crystal in steps on $0.25^\circ$ over a range of $100^\circ$. This measurement was conducted to ensure that no extraneous reflections are present which would suggest additional modifications to the magnetic structure,
relative to that of the parent compound. In addition to the bright (110) and (002) nuclear reflections, we find a series of peaks along the (0.5, 0.5, l) direction. Note that because of the small dimensions of the sample relative to the aluminum sample plate, a substantial background contribution is observed for parts of the map appearing as temperature-independent streaks or peaks of elevated intensity at larger “radii.”

The Néel temperatures $T_N$ for $x = 0.17$, 0.20, and 0.27 were extracted by fitting the integrated intensity of a representative magnetic reflection at $Q = G + q$, where $G$ is reciprocal lattice vector, with a mean-field order-parameter function denoted by the solid line. The best fits are denoted by the solid lines in Figs. 13(a)–13(c). The ordering temperatures are plotted in Fig. 14(b).

In contrast to the results for the other concentrations, the $x = 0.27$ sample exhibits commensurate order along the unit-cell diagonal described by a propagation vector $q = (0.5, 0.5, 0.5)$. No evidence for the incommensurate phase was observed along the (0.5, 0.5, l) direction as shown in the inset of Fig. 13(c).

For the compound with $x = 0.27$, a second transition $T_I$ below $T_N$ is observed in $C(T)$. However, neutron diffraction measurements show only one transition in this compound, described above as commensurate AFM order at $Q_N$, revealing that $T_I$ is unaccounted for in the neutron diffraction measurements. Possible reasons for this can be that the changes in the magnetic structure below $T_I$ are subtle, or that a different magnetic structure with a distinct propagation vector coexists with the identified commensurate order. Additionally, the inability to detect this potential propagation vector may suggest that the second modulation may have a miniscule magnetic moment. Finally, the transition $T_I$ may be associated with a different phenomenon such as a Lifshitz transition that reflects subtle changes in the electronic density of states. This may be related to changes in the hybridization of conduction- and $f$-electron states due to the observed valence change.

The difference in magnetic structure for Ce$_{1-x}$Yb$_x$RhIn$_5$ between the $x = 0.17$, 0.20, and 0.27 samples suggests that there is a crossover or transition from incommensurate to commensurate AFM order between $0.20 \leq x \leq 0.27$, which coincides with changes observed in the behavior of electrical resistivity, magnetic susceptibility, and specific-heat measurements for this concentration range.

IV. CONCLUDING REMARKS

A. Phase diagram

Shown in Figs. 14(a) and 14(b) are the Yb valence $v_{Yb}$ and the Néel temperature $T_N$ vs Yb concentration, respectively. Plots of these $v_{Yb}$ and $T_N$ vs $x$ are shown to emphasize a potential link between the magnetic structure of Ce$_{1-x}$Yb$_x$RhIn$_5$ and the valence of Yb. The incommensurate AFM phase appears to correspond to the region over which the Yb valence varies between 3+ and 2.1+, while the commensurate AFM phase appears when the Yb valence becomes stable at 2.1+.
as a function of $x$, we determined that the actual Yb concentrations $x_{\text{act}}$ are lower in our Ce$_{1-x}$Yb$_x$RhIn$_5$ single crystals than the nominal values $x_{\text{nom}}$. In contrast, results of similar chemical and structural analysis on polycrystalline samples of Ce$_{1-x}$Yb$_x$RhIn$_5$ showed $x_{\text{act}} \approx x_{\text{nom}}$. Using measurements of magnetic susceptibility and XANES, we estimated the Yb valence as a function of $x$. Just as has been observed in Ce$_{1-x}$Yb$_x$CoIn$_5$, we found that the Yb valence decreases as a function of $x$ until stabilizing at an intermediate valence of $2.1+ \approx x \approx 0.2$. Since the behavior of the valence of Ce$_{1-x}$Yb$_x$RhIn$_5$ is similar to that of Ce$_{1-x}$Yb$_x$CoIn$_5$, where there is also a Fermi surface reconstruction at $x = 0.07$ indicating an overall change in the electronic structure, it is reasonable to expect a Fermi surface reconstruction at $x = 0.2$ for Ce$_{1-x}$Yb$_x$RhIn$_5$. However, additional and difficult types of measurements such as Shubnikov–de Haas would need to be performed to confirm this scenario, although it could potentially provide an explanation for the observed magnetic phase transitions. Neutron scattering experiments demonstrate that the abrupt change in the $x$ dependence of the Yb valence near $x = 0.2$ coincides with a change in the magnetic structure from an incommensurate AFM ground state for $0 \leq x \leq 0.2$ to a commensurate AFM ground state for $0.2 < x < 0.27$. Heat-capacity measurements reveal that a second phase transition of magnetic origin emerges in this concentration range at a temperature $T_\text{f} < T_N$.

B. Discussion

The phase purity and crystal structures of Ce$_{1-x}$Yb$_x$RhIn$_5$ single crystals, synthesized using a molten In flux technique, were confirmed through Rietveld refinement analysis on powder XRD patterns. Given the well-documented subnominal Yb concentrations found in single crystals of the related system Ce$_{1-x}$Yb$_x$CoIn$_5$, we determined the actual Yb concentrations in our Ce$_{1-x}$Yb$_x$RhIn$_5$ single crystals using EDS and TXAS measurements. Combining the results from these measurements with a Vegard’s law analysis of the unit-cell volume

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