Local structure and site occupancy of Cd and Hg substitutions in CeTIn₅ (T=Co, Rh, Ir)

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The CeTIn₅ superconductors (T=Co, Rh, or Ir) have generated great interest due to their relatively high transition temperatures, non-Fermi liquid behavior, and their proximity to antiferromagnetic phase boundaries and quantum critical points. In contrast to small changes with the T-species, electron doping in CeT(In₁₋ₓMₓ)₅ with M=Sn and hole doping with Cd or Hg have a dramatic effect on the electronic properties at very low concentrations. The present work reports local structure measurements using the extended x-ray absorption fine-structure (EXAFS) technique that addresses the substituent atom distribution as a function of T, M, and x, in the vicinity of the superconducting phase. Together with previous measurements for M=Sn, the proportion of the M atom residing on the In(1) site, f_M(1), increases in the order M=Cd, Sn, and Hg, ranging from about 40% to 70% (random = 20%). These results also indicate that f_M(1) ranges from 70% to 100% for M=Hg in the order T=Co, Rh, and Ir. These fractions track the changes in the atomic radii of the various species, and help explain the sharp dependence of T_c on substituting into the In site. However, it is difficult to reconcile the small concentrations of M with the dramatic changes in the ground state in the hole-doped materials with only an impurity scattering model. These results therefore indicate that while such substitutions have interesting local atomic structures with important electronic and magnetic consequences, other local changes in the electronic and magnetic structure are equally important in determining the bulk properties of these materials.

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I. INTRODUCTION

The rich variety of novel strongly-correlated electron phenomena observed in the family of CeTIn₅ (T=Group VIII transition metal) heavy fermion compounds¹ such as the coexistence of unconventional superconductivity and magnetism under pressure²,³ or through chemical substitution,⁴,⁵ and magnetic field-induced magnetism within the superconducting state,⁶-⁸ has invigorated interest in understanding the interplay of superconductivity and magnetism in strongly-correlated materials. The CeTIn₅ family (generically referred to as the “115s”) is ideally suited to explore this interplay as the energy scales of these two ground states are easily tuned with modest pressures or magnetic fields. Recent work has focused on the effects of substitutions onto the In sites (Fig. 1), effectively either electron doping with Sn⁹ or hole doping with Cd¹⁰ or Hg.¹¹ Previous local structure studies of the atomic environment around the Sn atoms using the extended x-ray absorption fine-structure (EXAFS) technique found that the Sn atoms preferentially reside on the In(1) site, helping explain the sharp dependence of the superconducting (SC) transition temperature, T_c, on the Sn concentration and further supporting the notion of quasi-two-dimensional superconductivity confined primarily to the Ce-In(1) planes.¹² Subsequent studies have shown that hole doping produces even more dramatic effects, including accessing the antiferromagnetic (AFM) phase and exhibiting reversible behavior under applied pressure.¹⁰,¹¹ It is therefore vital to determine the distribution of Cd and Hg on the In sites in these samples in order to properly assess the role that impurity scattering plays in the properties of the hole-doped 115 materials. The present study extends the previous study on CeCo(In₁₋ₓSnₓ)₅ and determines these distributions using the EXAFS technique as a function of the species of M in CeCo(In₁₋ₓMₓ)₅ with M = Cd and Hg, and as a function of T in CeT(In₁₋ₓHgₓ)₅ with T = Co, Rh, and Ir.

FIG. 1: (Color online) The tetragonal unit cell of the Ce-115s.
The substitution of Cd or Hg for In at the percent level in CeTIn₅ has revealed a simple way to continuously tune between SC and AFM order (Fig. 2) while introducing minimal structural disorder. In particular, $T_c$ remains nearly constant with increasing Cd substitution up to $x=0.5\%$ from 2.3 K in pure CeCoIn₅. Superconductivity coexists with long-range AFM order for $0.5\% < x \leq 1.25\%$, after which point only AFM is observed.\(^{10}\) (Note that concentrations as measured by microprobe measurements of Cd and Hg are reported throughout this article, which are very close to 10% of the nominal concentration reported previously.\(^{11}\)) The entropy balance between these ground states along with the observation of coupled SC and AFM order parameters by neutron diffraction, implies that the same electronic degrees of freedom determine the nature of the ground state in these materials.\(^{13}\) The application of pressure to CeCoIn₅:Cd reverses the evolution of the ground state with Cd substitution and also mimics the pressure-induced behavior of CeRhIn₅,\(^{3}\) in which AFM order is suppressed from its ambient pressure value of $T_N = 3.8$ K to zero temperature by ~2.3 GPa, and coexists with superconductivity in an intermediate pressure range between 0.5 GPa and 1.7 GPa. However, for the small Cd concentrations that induce these changes, there is no detectable change in the average structure. Therefore, the effect of Cd substitutions on the electronic and magnetic properties only appear to act like negative applied pressure. These results suggest that it is the slight hole-doping of CeCoIn₅ with Cd that tunes the electronic structure sufficiently to induce magnetism, rather than chemical pressure or disorder effects.

This behavior contrasts with that achieved by electron doping with Sn into CeTIn₅, which uniformly suppresses AFM order in CeRhIn₅ by 7\% Sn for In without inducing superconductivity,\(^{9}\) and completely suppresses superconductivity in CeCoIn₅ at 3-4\% Sn with no sign of antiferromagnetic order.\(^{14,15}\) This behavior is more congruous with that achieved by substituting with La on the Ce site,\(^{16}\) especially when considering the propensity of Sn to rest on the in-plane In(1) site.\(^{12}\) Even so, the reduction of $T_c$ with the Sn In(1)-site occupancy remains sharper compared to La substitutions, providing further evidence that slight changes in electronic structure dominate the underlying physics in the substituted CeTIn₅ materials. Although Abrikosov-Gorkov-like\(^{12,17,18}\) pair-breaking undoubtedly plays some role, exactly how such minute quantities of these particular substituent atoms are able to tip the delicate balance between the nearly degenerate SC and AFM ground states in CeTIn₅, where substitution on the transition metal site requires of orindance effects.

Here, the local structure around Cd and Hg in CeTIn₅ using the EXAFS technique is reported to determine how the local environment affects the ensuing magnetism and superconductivity. The EXAFS technique, while only having a range of about 6 Å, provides a particularly powerful way of determining the local atomic environment around the substituent atoms, because a specific core-electron x-ray absorption process is chosen. Therefore, even though only percent fractions of Cd or Hg exist in a material, only scattering paths involving Cd or Hg contribute to the EXAFS signal. The main structural difference for differentiating between the In(1) and In(2) sites is the nearest-neighbor In(2)-$T$ distance at about 2.8 Å, since the nearest neighbors to the In(1) site are Ce and In(2) at about 3.3 Å. Other differences in the local structures around the In(1) and In(2) sites also help determine the fraction of the substituent atoms on the In sites. In addition, EXAFS is useful for determining distortions from the average crystal structure, which may also be important in determining the effects of substitutions onto the In sites.

The rest of this article is organized as follows: experimental methods and data fitting techniques are described in Sec. II, while the details of the results of the fits are in Sec. III. These results are related to various parameters in Sec. IV, such as $T_c$, the various atomic radii and the substituent In(1)-site occupancy. Finally, the main conclusions of this research are summarized in Sec. V.

FIG. 2: (Color online) Phase diagram of Cd- and Hg-substituted CeCoIn₅.
FIG. 3: Examples of $k$-space data at 30 K for representative samples at all four measured edges. These data are from averages of between 3 and 6 scans, each measured over about a half of an hour.

II. EXPERIMENTAL METHODS

Samples were synthesized as in Refs. 10, 11. X-ray diffraction measurements on the Cd-substituted samples indicate contraction of both the $a$ and the $c$ lattice parameters of about 0.005 Å in the vicinity of the critical concentration $x_c$ where the samples cease to be superconducting (Fig. 2). Measurements on the Sn- and Hg-substituted samples, however, have not been able to identify any clear trend in the lattice parameters with concentration. Microprobe analysis of $\text{CeCo(In}_{1-x}\text{Cd}_x)_5$ yielded an actual/nominal Cd concentration ratio $x_{act}/x_{nom} = 0.11$, close to the value of 0.10 reported in Ref. 10. A similar analysis$^{19}$ yielded an actual/nominal Hg concentration ratio of 0.16, 0.17, 0.18 for $T =$ Co, Rh, Ir, respectively. Lacking microprobe data for $\text{CeRh(In}_{1-x}\text{Cd}_x)_5$ and $\text{CeIr(In}_{1-x}\text{Cd}_x)_5$, the same actual/nominal Cd concentration ratio was used for a relative comparison to the Hg-doped $\text{CeRhIn}_5$ and $\text{CeIrIn}_5$ temperature-composition phase diagrams, given that Cd is isoelectronic with Hg.

The following samples were measured with the EXAFS technique for this study, although not all data are explicitly reported for the sake of brevity: $\text{CeCo(In}_{1-x}\text{Cd}_x)_5$ with $x=0.003$, 0.005, 0.011 and 0.18; $\text{CeCo(In}_{1-x}\text{Hg}_x)_5$ with $x=0.007$, 0.012, and 0.014; $\text{CeRh(In}_{1-x}\text{Hg}_x)_5$ with $x=0.009$, 0.026, and 0.035; and $\text{CeIr(In}_{1-x}\text{Cd}_x)_5$ with $x=0.009$, 0.018, and 0.036.

X-ray absorption data were collected at Beamline 11-2 of the Stanford Synchrotron Radiation Lightsource using half-tuned Si(220) monochromator crystals on the unfocused beam. The samples were prepared for these absorption measurements by grinding them in a mortar and pestle under acetone, with the resulting powder passed through a 32 µm sieve. This powder was brushed onto adhesive tape, which was then cut into strips and stacked, either in sufficient quantity to have reasonable fluorescence data from the Cd $K$ and Hg $L_{III}$ edges, or to obtain a change in the absorption across the In $K$ edge of about 0.8. The samples were placed in a liquid helium flow cryostat at 30 K. Data at the Cd $K$ or Hg $L_{III}$ edges were collected in fluorescence mode and corrected for the dead time of the 32-element Ge detector.

Data reduction and fitting were performed using the RSXAP package$^{20,21}$ with scattering functions generated by the FEFF7 code.$^{22}$ In particular, data collected in transmission mode must be treated differently than data collected in fluorescence mode. For the In $K$-edge data collected in transmission mode, the absorption contribution from the desired core excitation, $\mu_a$, was isolated by subtracting the contribution from other absorption processes as determined from a fit to the pre-edge data and forcing the remaining absorption to follow a Victoreen formula$^{23}$ ($\mu_a = \mu - \mu_{pre}$). The embedded atom absorption $\mu_0$ was generated by fitting a 7-knot cubic spline function through the data above the main absorption edge. The EXAFS function was then calculated using $\chi(k) = [\mu_a(k) - \mu_0(k)]/\mu_0(k)$, where $k = [2m_e(E - E_0)/h^2]^{1/2}$, $E$ is the incident photon energy, and $E_0$ is the photoelectron threshold energy as determined by the position of the half-height of the edge. Fluorescence data are treated similarly, but there are two important differences. First, the absorption processes from channels other than the desired excitation are already discriminated against by the energy-sensitive Ge detector, apart from much smaller correction due to roughly constant background processes and Compton scattering of the direct beam into the energy window for the desired Cd $K_a$ or Hg $L_a$ fluorescence lines. For each absorption process, a fluorescence photon is generated, so overall changes in the fluorescence above the absorption edge already should include the overall decrease in the absorption described by the Victoreen formula. For these reasons, a different pre-edge background, $\mu_{pre}$ is applied that only tries to isolate the desired fluorescence line. Second, self-absorption processes can play an important role, and are, in fact, the main factor in overall increases or decreases in the observed fluorescence.$^{24-26}$ A self-absorption correction$^{26}$ was applied, but was typically less than 2%. Examples of these data are shown.
in Fig. 3 as an indication of data quality. Note that all data were collected to 16.0 Å⁻¹ except the Hg LIII-edge (12284 eV) data for CeRh(In₀.93Hg₀.07)₅, which was limited to 11.5 Å⁻¹ by the Ir LIII edge (12824 eV).

The 115 local structure around Ce and T-site atoms is relatively simple, with well separated scattering shells. The local structure around In is much more complicated, owing both to the two In sites and to strong overlap between In(1)-Ce, In(1)-In(2), In(2)-In(2), In(2)-In(1), and In(2)-Ce near neighbors, all near 3.3 Å. Although substituent atoms should appear in the backscattering (for instance, the In(1)-In(2) peak will overlap an In(1)-Hg(2) peak), such scattering shells have an insignificant contribution at the measured substituent concentrations. Such peaks are, in any case, included in the fitting model. In all, there are 20 single scattering paths up to 5 Å. The bond lengths in the fitting model are therefore tightly constrained to the nominal 115 structure, equivalent to only allowing the a and c lattice parameters, the position z along the c axis of the In(2) sites, and, when the data allows, two additional atom-pair distances to vary. Only the Cd-edge data and the Hg-edge data on the substituted CeHg₅ sample required tightening these constraints. In addition, many of the mean-squared displacements of the pair distances (σ²’s) are also constrained together. The amplitudes are constrained to the nominal values, allowing both for an overall scale factor in the fit (S₀²), the fraction of the absorbing atom on the In(1) site (fIn(1)), and the x value for the substituent concentration, only the latter of which is held fixed. Note that only scattering paths with variable bond lengths are reported in the tables for simplicity, with one exception. The varied parameters that are not explicitly reported are σ² parameters. However, all of these fall within reasonable limits, never exceeding about 0.006 Å².

Reported errors are determined using a Monte Carlo method²⁷ that do not properly account for systematic errors. The possible magnitude of systematic errors are discussed in Sec. III below.

### III. RESULTS

Fourier transforms (FTs) of the $k^2\chi(k)$ data from the In K edge are shown in Fig. 4, which demonstrate several of the important features of the other transforms discussed in this article. The largest peak is due to several overlapping In-In and In-Ce pairs, as discussed above and indicated in the Tables. The peak position $r$ is shifted from the actual pair distance $R$ due to a phase shift of the photoelectron that occurs both as the electron leaves and returns to the absorbing atom and at the backscattering atom. This shift is well reproduced by FEFF7 and so accurate bond lengths can be obtained in the fits.²³ The real part of the transform (shown as the oscillating line between the modulus envelope in the FT figures) gives an indication of this phase shift as a function of the backscattering atomic species. In particular, Rh is both a stronger back-scatterer than Co, and has a much larger phase shift. Therefore, the In-Rh peak near $r \sim 2.5$ Å is larger, but nearly out of phase with the In-Co peak.

The varied parameters that are not explicitly reported in Table I for CeRhIn₅ are discussed in Sec. III below. The primary purpose of such fits is to demonstrate the efficacy of the fitting model, and therefore the final results are compared to the nominal crystal structure to help quantify any systematic errors. To this end, the measured pair distances are all close to those measured by diffraction, although outside the estimated errors. Considering that only 5 fit parameters describe all the bond lengths up to 5 Å, the systematic errors in the pair distances are expected to be within about 0.02 Å,²³ as observed. The σ² parameters are all small, as expected for a well-ordered crystal lattice. Of particular interest is the fraction of In atoms in the In(1) site, which is nominally 0.2. Within this fitting model, $f_{\text{In}(1)} = 0.12(5)$. The In K-edge fits to data from all the samples give similar results, so systematic errors in $f_{\text{In}(1)}$ are expected to be better than 0.1. However, this error may be smaller when more of a particular atom resides on the In(1) site, as is the case below.

The Cd K-edge fit results for three of the

| In(1)-Ce | 3.2923 | 0.47 | 0.0017(7) | 3.270(4) |
| In(1)-In(2) | 3.2775 | 0.94 | 0.0027(5) | 3.23(6) |
| In(2)-Rh | 2.7500 | 1.76 | 0.0023(3) | 2.736(2) |
| In(2)-Ce | 3.2775 | 1.76 | 0.0017(6) | 3.27(1) |
| In(2)-In(2) | 4.6142 | 0.87 | 0.001(1) | 4.64(1) |

$\Delta E_0 = -5.6(6)$
$S_0^2 = 0.94(6)$
$f_{\text{In}(1)} = 0.12(3)$
$R(%) = 6.13$

²⁷From Ref. 29 for CeRhIn₅
²³Constrained to In(1)-Ce
CeCo(In$_{1-x}$Cd$_x$)$_5$ samples are summarized in Table II, and an example of the fit for \( x=0.011 \) is shown in Fig. 5a. Two extra constraints were necessary on the bond lengths due to the distortion discussed below, and the maximum \( r \) in the fit range was limited to \( 5.1 \) Å in order to reduce the effect of multiple scattering on determining this distortion. The fit model describes the data very well, with \( f_{\text{In}}(1) = 0.47(4) \) for the \( x=0.011 \) sample. No obvious trend in \( f_{\text{In}}(1) \) is observed with \( x \), and a value of \( f_{\text{In}}(1) = 0.43(3) \) describes the fits to all the Cd-substituted samples. One can get a rough estimate of the number of Cd on In(2) sites by comparing the FT data in Fig. 5a to the In K-edge data in Fig. 4a. These data show a reduction in the amplitude of the peak near \( r = 2.5 \) Å of \( \sim 80\% \) of the same peak from the In edge, indicating \( 0.8 \times 4/5 \approx 64\% \) of the Cd sit on In(2) sites, or about 36\% on In(1) sites, in rough agreement with the fits. The most obvious difference, however, is in the amplitude of the further peaks. Although these can be fit by including lattice disorder via enhanced \( \sigma^2 \) parameters with an \( R(\%) \) of about 18.4\%, the fit quality is substantially improved by allowing for a local contraction of about 0.2 Å of the \( c \) axis near Cd atoms. The \( c \) axis in the fit in Table II is \( 7.32(3) \) Å, compared to the CeCoIn$_5$ value from diffraction\(^{29} \) of \( 7.5513 \) Å. Meanwhile, \( a = 4.602(7) \) Å and \( z = 0.297(7) \) (position along \( c \) of In(2) plane) from these Cd \( K \) edge fits, in reasonable agreement with the values from diffraction in CeCoIn$_5$ of \( c_{\text{diff}} = 4.6129 \) Å and \( z_{\text{diff}} = 0.3094 \). As a consequence of this \( c \) axis distortion, the overlapping Cd(1)-Ce, Cd(1)-In(2), In(2)-Ce, etc., peak positions are split by \( \sim 0.1 \) Å, causing the dominant peak in the In edge FTs in Fig. 4a to be strongly suppressed in the Cd edge FTs in Fig. 5. The same argument holds for the further peaks.

Data and fit results to the other Cd-substituted samples are similar, in spite of the obvious, and apparently systematic, differences in the transforms shown in Fig. 6. These differences are described well by the fit parameters shown in Table II as being mostly due to differences in the mean-squared distribution widths, \( \sigma^2 \), for the various...
peaks. In particular, no trends are observed in $f_{\text{In}(1)}$.

By comparison, the Hg-edge data are much more straightforward. Unlike both the Cd- and Sn-substituted CeCoIn$_5$ samples, Hg appears to substitute much more strongly onto the In(1) site, with $f_{\text{In}(1)} \approx 70\%$ (see Table III). For $T=$Rh, Hg sits almost uniformly on the In(1) site, with little change to the local lattice. This result is clearly visible both in the data and fits shown in Figs. 5b and 7a, and in the fit results in Table III. A strong correlation exists in the fits between the $\sigma^2$ parameters from the Hg(2) sites and $f_{\text{In}(1)}$, whereby a large Hg(2) $\sigma^2$ reduces $f_{\text{In}(1)}$. Such a correlation is expected for high $f_{\text{In}(1)}$, since very little, if any, of the EXAFS signal will be coming from the Hg(2) sites, and EXAFS amplitudes go as $1/\sigma$. Some of these Hg(2) $\sigma^2$ parameters had to be limited to 0.04 Å$^2$ in the fits to keep them from being arbitrarily large. Data and fit results on the other CeRh(11−$x$Hg$_x$)$_5$ samples are similar, with $f_{\text{In}(1)} = 0.92(4)$. 

Fit results on CeIr(11−$x$Hg$_x$)$_5$, while consistent with 100% of the Hg on In(1) sites, are of lesser quality (Fig. 7b) with a much larger $R(\%)$ value (Table III), possibly indicating that not all of the Hg substitutes into the CeIrIn$_5$ lattice. Preliminary nuclear quadrupole resonance (NQR) data also show that not all of the Hg is in a simple In-like site in the crystal lattice. A strong possibility is that a small fraction of the Hg exists in another phase, probably some kind of Hg-In binary alloy, although including scattering paths from common Hg-In alloys, such as HgIn, did not improve the fit quality. It is important to recall that EXAFS selects the Hg atoms, even though they only exist in about 1% of the lattice, and so a possible 20% Hg-phase fraction would only translate to 0.2% of the sample, yet still account for the misfit in the Hg-edge data. In any case, there remains no evidence of a Hg-Ir peak near 2.8 Å, indicating none of the Hg sits on the In(2) site.
The difference in the local environment around the In(1) and In(2) sites is substantial, with a nearest-neighbor pair distance of half an angstrom shorter from the In(2) site. It is therefore not surprising that a given substituent onto the In sites would prefer the In(1) site, and, in fact, the measured distributions track the atomic radii both of the substituent species $M$ and of the transition metal species $T$. Specifically, the calculated radii for In is 2.00 Å, while for Cd, Sn, and Hg, it is 1.71 Å, 1.72 Å, and 1.76 Å, respectively. These values track the respective occupancies $f_{\text{In}(1)}$ in CeCo(In$_{1-x}$M)$_5$ of 43(3)%, 55(5)%, and 71(5)%, assuming no dependence on $x$. The occupancies $f_{\text{In}(1)}$ in Ce$T$(In$_{1-x}$Hg$_x$)$_5$ also track how constricted the In(2) environment is by the $T$ species: the atomic radii of Co, Rh, and Ir, are 1.67, 1.83, and 1.87 Å, respectively, a situation that is also reflected in the measured In(2)-$T$ distance in the average crystal structures of Ce$T$In$_5$. It is worth pointing out that this situation is not unique in anisotropic crystal structures with two very different sites for a given atomic species. For example, there are two Cu sites in YBa$_2$Cu$_3$O$_7$, and substitutions of Cu with Co are almost uniformly on the chain Cu(1) site (eg. see Refs. 32 and 33).

The effect of placing the impurity preferentially into the Ce-In(1) plane undoubtedly affects the progression of SC and AFM phases with $M$ concentration, $x$. This point has been argued with respect to Sn substitutions, where it was found that $T_c \rightarrow 0$ K roughly when the mean separation between impurities within a plane is about equal to the superconducting coherence length in the pure material. Although this may be the dominant effect in rapidly reducing $T_c$ with respect to $x$, more subtle effects likely determine the variation between samples with Cd, Sn, and Hg substitutions in CeCoIn$_5$. For one, even though $f_{\text{In}(1)}$ is slightly smaller for Cd substitutions compared to Sn, superconductivity is destroyed more quickly with $x$ for Cd than Sn (Fig. 2). One can argue that this difference is due to the fundamental Ce/In charge interaction differences between these materials, since one is hole doped while the other is electron doped. In that case, one should directly compare the hole-doped, Cd- and Hg-substituted systems. The ratio between the critical concentrations, $x_c$, where superconductivity is destroyed between Cd (1.7%) and Hg (1.4%) is about 1.2. This value is close to the square of the ratio of $f_{\text{In}(1)}$ for Hg and Cd of about 1.3, further supporting the notion of strong scattering for the in-plane In(1)-site impurities. Although this argument seems to explain differences in $x_c$ based on $f_{\text{In}(1)}$, it doesn’t explain all the differences between Cd and Hg substitutions in CeCoIn$_5$. For instance, $T_c$ is higher for all $0.8 < x < 1.4\%$ in Hg-substituted...
samples compared to Cd-substituted samples, despite the much higher In(1) occupancy of Hg. These results indicate that while qualitatively the degree of In(1)-site occupancy plays a role, the detailed electronic structure around an impurity is at least as important in determining quantitative behavior and possible role of a “local pressure” effect around the $M$ atom.

The effect of structural disorder on the electronic and magnetic properties introduced by percent-level substitutions on the In sites remains enigmatic. The central dichotomy is between the observations of dramatic changes in the ground-state properties and the small changes in the lattice parameters. In fact, one expects less than 0.004 Å reduction in the lattice parameters at $x_c$ based on the atomic radii. Diffraction measurements (Sec II) on the Cd-substituted material indicate a lattice contraction consistent with this value. Measurements on the Sn- and Hg-substituted samples, however, have not been able to identify such a contraction. In any case, such a small distortion should have a relatively small effect on the magnetic coupling strength $J_\varrho$, where $J$ is the local moment/conduction electron exchange parameter and $\varrho$ is the electronic density of states at the Fermi level. For instance, $J \propto V_f^2$, the hybridization matrix element, which goes as $1/R^5$ in a tight-binding model,\cite{34,35} where $R$ is the distance between the Ce and In atoms. This formula implies a less than 1% increase in $V_{fc}$. Countering this change, the $p$-electron orbital radius of all the substituents discussed here causes an overall decrease in $V_{fc}$ with $x$ relative to the pure compound. Similarly, even if each substituent changes the local density of states by 50%, the average change would be less than 1% at $x_c$, positive for Sn and negative for Cd and Hg. Consequently, $J$ should be nearly constant for Sn and decrease by less than 2% for Cd and Hg. Because of these small changes in the average structure and conduction electron concentrations, it is difficult to rationalize the dramatic changes in the ground state in these materials, even if one argues that the undoped system lies near a sharp band. One can argue\cite{12} that the SC state is very sensitive to small amounts of disorder; however, such an argument can’t easily apply to the sharp increase in $T_N$ observed in the Cd and Hg substituted samples. In any case, there are other indications that the electronic structure is remarkably sensitive to small local structure changes. For example, Dynamical Mean Field Theory calculations on CeIrIn$_5$ indicate that the hybridization of the Ce-In(2) bond is stronger than that of the Ce-In(1) bond despite nearly equal bond distances, giving rise to two hybridization gaps in the optical conductivity at ~30 meV and ~70 meV, in agreement with experiment.\cite{36}

A clue for resolving this issue of how the In-site substituents control the physics of the CeTIn$_5$ compounds comes from recent NQR experiments on Cd-substituted CeCoIn$_5$.\cite{37} The In NQR data taken on pure CeCoIn$_5$ (SC only), 1% (coexistent AFM and SC order), and 1.5% (only AFM) Cd-substituted samples indicate that the changes in electronic structure occur locally around a substituent atom. This conjecture is supported by NQR data in the normal state, which show that the spin-lattice relaxation rate is nearly identical despite radical changes in the ground state. It is expected that large changes in the spin-fluctuation spectrum, and hence $1/T_1$, should occur in the evolution from a SC to an AFM state, and is observed in systems such as CeCu$_2$(Si,Ge)$_2$.\cite{38} However, if Cd nucleates magnetism on a scale less than the magnetic correlation length, for instance, by changing the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction through a change in $\varrho$ or $J$, then there will be little change in $1/T_1$. Only when the substituent concentration is large enough such that the magnetic correlation lengths overlap does long-range order develop. For the sake of argument, consider only correlations in the $ab$ plane and Cd atoms on the In(1). Long-range antiferromagnetic order develops at about $x = 0.8\%$, or about 0.5% of the In(1) sites occupied with Cd. The mean separation between Cd atoms along the a or b directions is therefore about 14 lattice spacings. Inelastic neutron scattering measurements on CeCoIn$_5$ reveal\cite{39} that the dynamic correlation length in the $ab$ plane is about $\xi_{ab} = 9.6$ Å, which is only about 2 lattice spacings. The antiferromagnetic droplets would then have to increase 7-fold in this simplified two dimensional model to overlap and generate long-range magnetic order. Nuclear Magnetic Resonance measurements, in fact, show indications of such an increase in $\xi$ below 10 K in a Cd-substituted sample.\cite{40}

The picture that is emerging is reminiscent of the Kondo disorder\cite{41,42} and antiferromagnetic Griffiths’ phase\cite{43} discussions around compounds like UCuPd and U$_{1-x}$Y$_x$Pd$_3$.\cite{44} These arguments revolve around the magnetic coupling strength $J_\varrho$, and the Doniach argument regarding the competing effects of the Kondo interaction and the RKKY effect.\cite{45} Here, the reduction of $T_c$ in the electron-doped material occurs due to the distribution of scattering centers and the strong Abrikosov-Gorkov-like (AG) scattering mechanism,\cite{17} only requiring local increases in the Kondo temperature around a scattering center.\cite{12} In the hole-doped, Cd- and Hg-substituted systems, $\varrho$ changes with $x$, apparently enough to allow RKKY interactions to dominate over the Kondo effect, potentially allowing antiferromagnetic droplets to form within a Griffiths’ mechanism around impurity sites, consistent with the NQR observations.\cite{37} Within this picture, in both the electron-doped, Kondo-disorder/AG, regime and the hole-doped, AF Griffiths phase regime, lattice disorder plays a key role in the development of various properties with $x$ by allowing the precipitation of larger-scale perturbations, either by disturbing the coherence of the large SC state or by precipitating long-range magnetic interactions. Although these qualitative ideas may indeed play a defining role in determining the properties in substituted 115s, a quantitative theory has not yet been developed that properly accounts for the details of this quantum critical system.
V. CONCLUSION

The fraction of $M$ atoms on In(1) sites is determined in CeT(In$_{1-x}$M$_x$)$_5$ as a function of $M$ in CeCo(In$_{1-x}$M$_x$)$_5$ and as a function of $T$ in CeT(In$_{1-x}$M$_x$)$_5$ with $T = $ Co, Rh, and Ir, using EXAFS measurements at the In K, Cd K, and Hg L$_{III}$ edges. Fits to the In K-edge data indicate no measurable change in the average structure with these substituents. Fits to the Cd K-edge data for CeCo(In$_{1-x}$Cd$_x$)$_5$ indicate about $f_{\text{In(1)}}=43(3)$% of Cd atoms reside on In(1) sites, independent of $x$ and similar to previous results$^{12}$ of $f_{\text{In(1)}}=55(5)$% for Sn in CeCo(In$_{1-x}$Sn$_x$)$_5$. In addition, the local lattice is distorted around Cd sites, consistent with a local decrease in the $c$ axis of about 0.2 Å, while the $a$ lattice constant and the $z$ parameter describing the position of the In(2) planes remain unchanged. These results contrast with those from the Hg L$_{III}$-edge data that indicate $f_{\text{In(1)}}=71(5)$% in CeCo(In$_{1-x}$Hg$_x$)$_5$, with only minimal changes to the local lattice structure. Moreover, $f_{\text{In(1)}}$ increases to 92(4)% for $T=$Rh and 100(10)% for $T=$Ir. While these results are rationalized in terms of the atomic radii of the $M$ and $T$ species and gross changes in the superconducting transition temperature, the dramatic changes in the ground state, especially in the hole-doped materials, are difficult to understand in terms of localized impurity scatterers. Rather, a sharper division can be made based on electron- versus hole-doped samples and allowing for the possibility of antiferromagnetic droplet formation. Therefore, while strong conduction electron scattering around In(1)-site defects undoubtedly plays a large, and possibly majority, role in the progression of $T_c$ with $x$, a complete understanding of the differences in the ground states requires a more thorough understanding of the actual electronic structure around defect atoms and their effect on the system as a whole.

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