Perturbing the Superconducting Planes in $CeCoIn_5$ by Sn Substitution

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In contrast to substitution on the Co or Ce site, Sn substitution has a remarkably strong effect on superconductivity in $CeCoIn_{5-x}Sn_x$, with $T_c \rightarrow 0$ beyond only ~3.6% Sn. Instead of being randomly distributed on in-plane and out-of-plane In sites, extended x-ray absorption fine structure measurements show the Sn atoms preferentially substitute within the Ce-In plane. This result highlights the importance of the In(1) site to impurity scattering and clearly demonstrates the two-dimensional nature of superconductivity in $CeCoIn_5$.

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With the discovery of unconventional superconductivity (SC) in $CeMIn_5$ (M = Co, Rh, or Ir), the study of the interplay between magnetism and SC has received much attention in the past few years. Various investigations have revealed that both SC and magnetic order coexist in $CeCo_{1-x}Rh_xIn_5$ and $CeIr_{1-x}Rh_xIn_5$ systems at ambient pressure over a wide range of concentrations [1–4]. There is also growing experimental evidence that these compounds are close to an antiferromagnetic quantum critical point in Doniach's phase diagram, and that SC is mediated by magnetic fluctuations with an anisotropic superconducting gap, possibly even with *d*-wave symmetry [5–8]. Here, we address the nature of SC by directly perturbing the superconducting state in $CeCoIn_5$.

$CeCoIn_5$ is an ambient pressure superconductor that crystallizes in the $HoCoGa_5$-type tetragonal structure with a superconducting transition temperature T_c = 2.3 K [9]. This structure (Fig. 1 inset) can be thought of as a layered version of $CeIn_3$, a pressure-induced superconductor with a maximum T_c of 0.2 K [10]. The order-of-magnitude increase of T_c in $CeCoIn_5$ has been attributed to its quasi-two-dimensional (2D) structure [6,9]. In fact, a local density approximation calculation finds no relevant hybridization of cobalt *d* orbitals with cerium *f*-band states, suggesting that the material can be thought of as a double-layered compound with two almost independent structures [11] as suggested by Shishido *et al.* [12]. Furthermore, average charge correlations between Ce and In(1) are higher than between Ce and In(2) in this calculation [11], implying a tendency toward 2D electronic dynamics in two dimensions. Measurements of the de Haas–van Alphen effect also reveal a cylindrical Fermi surface, much more 2D-like than either $CeIrIn_5$ or $CeRhIn_5$, suggesting that the increasingly 2D electronic structure has a direct correlation with enhanced T_c [13,14].

In addition, solutions of Eliashberg equations suggest that in magnetically mediated superconductors quasi-2D structures are favored over 3D systems [15]. More evidence for the role of dimensionality in determining T_c in the 115 compounds comes from crystallographic studies. A clear correlation between the c/a ratio and T_c has been observed in $CeM_{1-x}N_xIn_5$ (M, N = Ir, Rh, Co) and in the structurally related Pu-115 compounds [16–18]. Finally, critical field measurements in the (110) plane also suggests a 2D superconducting state in $CeCoIn_5$ [19].

Although this body of work provides strong circumstantial evidence for a 2D superconducting state, much of the evidence relates to the total Fermi surface, rather than to the superconducting piece. Some experimental work, however, aims at perturbing the superconducting state within the Ce-In planes, such as the c/a ratio and the critical field studies. Site substitution offers the ability to perturb the superconducting state at particular sites in the unit cell. For instance, substitution onto the Co site has a relatively small effect on T_c, with SC persisting at least up to 75% Rh in $CeCo_{1-x}Rh_xIn_5$ [16]. This situation is in contrast to substituting La for Ce, where SC is observed only up to 15% La substitution [20]. No technique has as yet perturbed the In sites and thereby focused on the effect of the *f*-electron local interactions. A possible route to

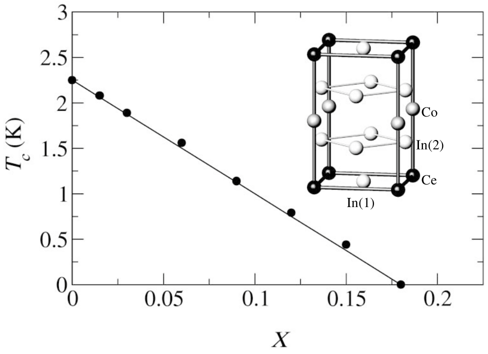

FIG. 1. Superconducting transition temperature from specific heat data [21] as a function of x in $CeCoIn_{5-x}Sn_x$. The inset shows the crystal structure of $CeCoIn_5$.

such studies would be to selectively substitute atoms onto the planar In(1) site.

A recent study by Bauer *et al.* [21] shows that SC in the $\mathrm{CeCoIn}_{5-x}\mathrm{Sn}_x$ alloy is destroyed after only ~3.6% Sn for In, or $x = 0.18$ (Fig. 1). This suppression is not due to a difference in the c/a ratio, since that ratio in $\mathrm{CeCoIn}_{5-x}\mathrm{Sn}_x$ is constant with x [21]. This result clearly suggests that there is a direct perturbation of the superconducting state with the replacement of Sn for In. The alloy $\mathrm{CeCoIn}_{5-x}\mathrm{Sn}_x$ is therefore an ideal system to explore the nature of SC in Ce-115 compounds. Moreover, it remains unclear why substituting on such a small percentage of In sites, only 20% of which are in the Ce plane, has such a large effect, especially compared to La substitution. In order to shed light on the mechanism by which SC is suppressed, we have carried out local structure investigations around the Sn atoms in $\mathrm{CeCoIn}_{5-x}\mathrm{Sn}_x$ using the extended x-ray absorption fine structure (EXAFS) technique. This technique utilizes the region in the absorption spectrum beyond ~10–20 eV above the absorbing edge, which contains information about the radial pair-distance functions around the absorbing species. We report Sn K-edge EXAFS measurements on $\mathrm{CeCoIn}_{5-x}\mathrm{Sn}_x$ ($x = 0.09, 0.12, 0.18$, and 0.24) and discuss the results in relation to the observed bulk properties.

Details of sample growth and characterization are described elsewhere [9,21,22]. Sn K-edge absorption spectra were measured in fluorescence mode with a half-tuned double-crystal Si(220) monochromator at beam line 11-2 of the Stanford Synchrotron Radiation Laboratory (SSRL). The single crystal samples were ground with a mortar and pestle and passed through a 20 μm sieve. The powdered material was then brushed onto adhesive tape and several layers were stacked together. The samples were mounted in a liquid helium flow cryostat and data were recorded at 30 K.

The EXAFS data were analyzed using the RSXAP software package [23–25] similarly to Ref. [26]. After preedge subtraction, the EXAFS function $\chi(k)$ was extracted from the measured absorption coefficient $\mu(k)$ according to $\chi(k) = \mu(k)/\mu_0(k) - 1$, where $\mu_0(k)$ is a smooth background function, the photoelectron wave vector $k = \hbar^{-1}[2m_e(E - E_0)]^{1/2}$, m_e is the electron rest mass, E is the incident energy, and E_0 is the threshold energy. The Sn concentration was low enough that correcting the data for self-absorption effects was not necessary. Structural refinements of the EXAFS data were performed in R space by fitting data to theoretical standards generated by FEFF7 [27]. Representative k-space data are shown in Fig. 2.

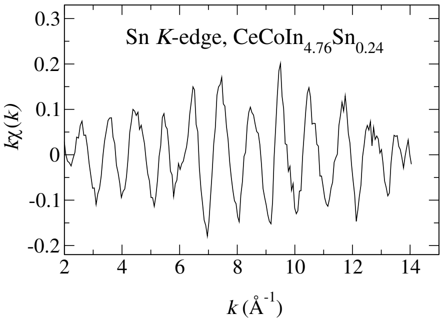

FIG. 2. $k\chi(k)$ data for $\mathrm{CeCoIn}_{4.76}\mathrm{Sn}_{0.24}$ at 30 K.

The EXAFS oscillations are determined by the local structure around the absorbing atomic species. Indium atoms at the planar In(1) site are surrounded by 4 Ce and 8 In near neighbors, at distances 3.268 and 3.286 Å, respectively [22]. On the other hand, Indium atoms at the low symmetry In(2) site have 2 Co and 1 In immediate near neighbors at 2.723 and 2.879 Å, respectively, followed by 4 In's at 3.268 Å, and 2 In and 2 Ce neighbors at a distance 3.286 Å. To help us compare the difference between the two sites, we have generated a theoretical EXAFS function $\chi(k)$ for each site. The Fourier transform (FT) of the simulated EXAFS function for both sites is presented in Fig. 3(a). Note that in the low R region for the In(2) site, there is a well resolved peak at ~2.4 Å (labeled A), which is mainly due to the 2 Co and 1 In near neighbors (due to the phase shift of the photoelectron at the absorbing and backscattering atoms, the peak positions are shifted by small known amounts from the actual pair distances). In addition, the peak at ~3.0 Å (labeled B), which is due to Ce and In neighbors, is larger for the In(1) site since it has more neighbors contributing to that peak, namely, 4 Ce's and 8 In's, compared to the In(2) site, which has 2 Ce and 6 In neighbors at this distance. Figure 3(b) compares the FT for In K-edge CeCoIn_5 data with Sn K-edge

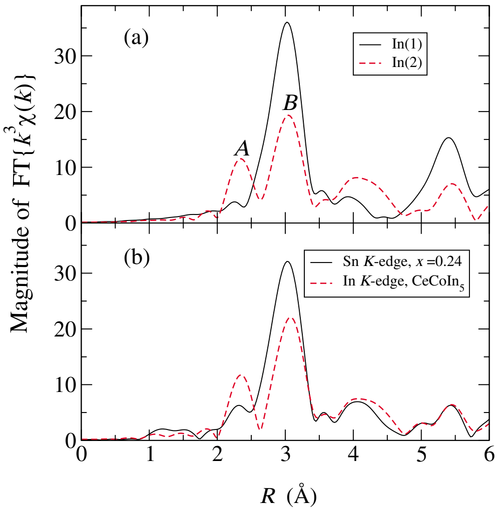

FIG. 3 (color online). (a) FEFF7 simulations of the magnitudes of the FT of $k^3\chi(k)$ from the In(1) and In(2) sites, using a correlated-Debye temperature of 161 K [37]; (b) FT's for In K-edge data from CeCoIn_5 and Sn K-edge data from $\mathrm{CeCoIn}_{4.76}\mathrm{Sn}_{0.24}$. FT's are between 3.0–14.0 Å^{-1}, Gaussian narrowed by 0.3 Å^{-1}.

$CeCoIn_{4.76}Sn_{0.24}$ data. The A peak is clearly larger and the B peak smaller in the parent compound than in the Sn-substituted one. These data therefore qualitatively indicate that fewer Sn atoms reside on the In(2) sites than expected from a random distribution over all available In sites.

The fraction of Sn atoms going to the In(1) site has been estimated by fitting the EXAFS signal to a linear combination of standards generated for the two sites (Fig. 4). The overall amplitude reduction factor S_0^2, the coordination distances R, and the pair distribution widths (σ's) were also allowed to vary. Only single scattering paths were included. Consistent with the observed FT features, the fit results show a major fraction of Sn predominantly occupying the In(1) site. Despite the fact that there are 4 times as many In(2) sites as In(1) sites, the fraction of Sn atoms going to the In(1) site is 0.6(1), 0.6(1), 0.5(1), and 0.6(1) for $x = 0.09$, 0.12, 0.18, and 0.24, respectively. With the exception of the Sn(2)-Co pair distance, which shows a 0.05–0.09 Å contraction, all other pair distances for the In(1) and In(2) sites agree with previously reported values for $CeCoIn_5$ [22,28].

Our findings are particularly significant when one considers the observed bulk physical properties of Sn-substituted $CeCoIn_5$ samples. In particular, these results help explain the much larger effect of Sn substitution as opposed to Rh or Ir substitution on T_c. In a three-dimensional superconductor, Abrikosov-Gorkov (AG) impurity scattering [29] would be similar for, say, Rh and Sn substitutions. However, our local structure studies show that Sn preferentially substitutes onto the Ce-In planes, which should enhance the impurity scattering in a 2D superconductor. One effect of this Sn distribution is to decrease the mean distance between Sn(1) impurities as compared to the superconducting coherence length ξ_a, which has been estimated to be $\approx$81 Å in $CeCoIn_5$ [14,30], or about 17–18 unit cells. If Sn were randomly distributed on the two In sites, the nearest distance between Sn(1) atoms would be about 120 Å, which should have only a small impact on T_c. Instead, our results indicate that the distance between Sn(1) atoms is about 50 Å, or about 11–12 unit cells. This impurity separation is within the estimate of ξ_a, and hence should have a large effect on T_c.

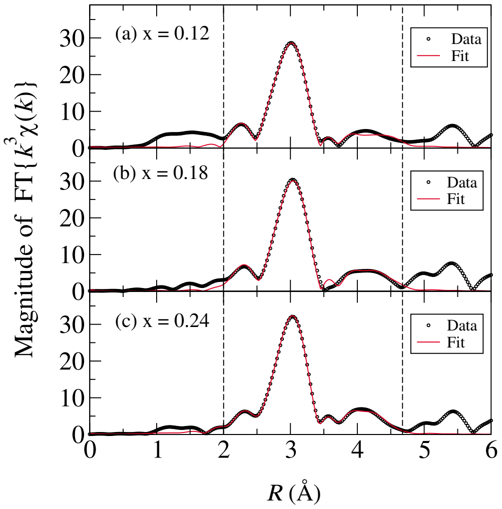

FIG. 4 (color online). Sn K-edge FT's from $CeCoIn_{5-x}Sn_x$ for various Sn contents. The fit range, 2.0–4.67 Å, is indicated by the dashed vertical lines.

The Sn-substitution situation is much more similar to substituting La for Ce. However, despite modifying the Ce-In plane, La has a less dramatic effect on SC as compared to Sn substitution [20]. This fact strongly suggests that Sn substitution induces an additional scattering mechanism in the Ce-In planes. Since AG-impurity scattering is enhanced by scattering off Kondo singlets [31], it is easy to imagine that Sn impurities strongly increase T_K as occurs in $CeIn_{3-x}Sn_x$ [32,33], as opposed to removing the Kondo singlet by La substitution. In fact, the temperature at which the electrical resistivity is a maximum is observed to increase with Sn concentration, indicating a probable increase in T_K [21]. However, it is not clear *a priori* whether Sn substitution should increase or decrease T_K. T_K is commonly given by $k_B T_K \approx E_F \exp(-\epsilon_f/V^2\varrho)$, where k_B is Boltzmann's constant, V is the local-moment/conduction-electron hybridization matrix element, ϵ_f is the f-level energy below the Fermi-level, and ϱ is the electronic density of states at the Fermi-level E_F. Therefore an increasing T_K implies either an increasing E_F, ϱ, or V, or a decreasing ϵ_f. It is difficult to predict the effect of Sn substitution on E_F and ϵ_f. In the tight binding formalism the hybridization strength between the Ce f and the In (or Sn) p electrons is of order $V_{fp} \sim (r_f^{5/2} r_p^{1/2})/d^5$, where r_p and r_f are tabulated electron wave function radii for a particular atom and d is the distance between the atoms [34]. Sn has a smaller r_p value than In [35], so V_{fp} should be weaker in the Sn-substituted material, and hence should decrease T_K [34]. On the other hand, Sn has one more p electron than In, so an increased conduction density of states in the Sn-substituted material may be responsible for the observed increase in T_K, similarly as suggested for $CeIn_{3-x}Sn_x$ [32].

Although magnetic impurities are usually considered as a pair-breaking mechanism, in a magnetically mediated superconductor T_c increases with the spin-fluctuation temperature, T_{sf} [15], and since T_K is a measure of T_{sf}, one might expect the opposite behavior compared to AG scattering. Instead, while T_K likely increases in $CeCoIn_{5-x}Sn_x$ and decreases in $Ce_{1-x}La_xCoIn_5$ [20] with increasing x, T_c decreases in both cases. It is important to note, however, that AG scattering is an impurity effect while the spin fluctuations responsible for magnetically mediated superconductivity are not. This decrease in T_c is therefore likely due to an AG-like impurity mechanism in addition to the spin-fluctuation mechanism for superconductivity. In this sense, local changes in the coupling parameters would cause pair breaking by directly perturbing the pairing mechanism.

These local perturbations may even generate a distribution of T_K's (similar to a Kondo disorder model [36]).

To summarize, the local structure around Sn in $\mathrm{CeCoIn}_{5-x}\mathrm{Sn}_x$ ($x = 0.09$, 0.12, 0.18, and 0.24) has been probed by EXAFS. Our fit results show that the majority of Sn atoms preferentially reside on the planar In(1) sites. Impurity scattering is therefore primarily confined to the Ce-In planes, in contrast to substituting with Rh or Ir, which substitute outside of this plane. This result implies that the impurity separation is much shorter than one would obtain by a random distribution of Sn atoms on In sites, and in fact one obtains a separation distance within the estimate of the superconducting coherence length ξ_a in CeCoIn_5 [14,30]. Our results further show that compared to La substitution onto the Ce sites, Sn substitution increases the planar scattering more effectively and this might be due to an increase in the Kondo singlet scattering. Taken together, these results indicate that the rapid suppression of T_c in $\mathrm{CeCoIn}_{5-x}\mathrm{Sn}_x$ is due to an enhanced perturbation of a superconducting state that is confined within the Ce-In planes, consistent with the 2D-like electronic structure of CeCoIn_5.

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