

Annealing, lattice disorder, and non-Fermi-liquid behavior in UCu_4Pd

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The magnetic and electronic properties of non-Fermi-liquid UCu_4Pd depend on annealing conditions. Local structural changes due to this annealing are reported from U L_{III} - and Pd K -edge x-ray-absorption fine-structure measurements. In particular, annealing decreases the fraction of Pd atoms on nominally Cu $16e$ sites and the U-Cu pair-distance distribution width. This study provides quantitative information on the amount of disorder in UCu_4Pd and allows an assessment of its possible importance to the observed non-Fermi-liquid behavior.

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The $\text{UCu}_{5-x}\text{Pd}_x$ system displays many of the canonical behaviors of other non-Fermi-liquid (NFL) systems.¹ For instance, at low Pd concentrations, x , it is an antiferromagnet (AF), with the Néel temperature, T_N , decreasing with increasing x . Near $x \approx 1$, T_N is reduced toward zero² and the magnetic and electronic properties become that of a NFL: the low-temperature linear coefficient of the specific heat and the magnetic susceptibility diverge logarithmically [$\gamma = C/T \propto \chi(T) \propto \ln(T)$] or as a weak power law over a more limited temperature range.³ Unannealed samples also exhibit NFL behavior in the resistivity with $\rho(T) - \rho_r \propto T$.

These observations suggest a possible quantum critical point (QCP) (Refs. 1, 4, and 5) as the cause of the NFL behavior. Subsequent research found that the aforementioned behavior can also be explained with a Kondo disorder model (KDM), consisting of a broad distribution $P(T_K)$ of Kondo temperatures, T_K , which extends down to very low temperatures.^{6,7} Inhomogeneous broadening of the copper nuclear magnetic resonance (NMR) line was taken as evidence for such a distribution,⁶ and lattice disorder was identified as its possible microscopic origin:⁸ Pd and Cu atoms were found to interchange positions within the $C15b$ ($F\bar{4}3m$) lattice, even for UCu_4Pd , which previously was thought to possess a well-ordered structure.

In spite of the arguments supporting the KDM, there is strong evidence that this simple model does not contain all the necessary elements to explain the experimental data. Inconsistencies include the anomalously fast muon spin-lattice relaxation rates measured by μSR in a longitudinal field,⁹ and the measurements of the spin-lattice relaxation rate at moderately high fields (> 51 kOe)¹⁰ from NMR down to 400 mK in $\text{UCu}_{3.5}\text{Pd}_{1.5}$. In addition, using lattice disorder as the microscopic origin for the breadth of $P(T_K)$ within a tight-binding description for the hybridization strength and a constant electronic density of states has been shown to require a continuous, nonthermal distribution in the near-neighbor uranium pair distances,⁸ which has not been observed.¹¹ Other theories that combine critical points with disorder phenomena¹² may eventually explain all the different data, and recent work considering a Kondo/quantum spin-glass critical point is also promising.¹³

Despite the evidence against the KDM as a “minimal model” describing NFL behavior in this material, the evidence still indicates that disorder plays an important role. This role is perhaps best exemplified by the series of experiments¹⁴ on annealed samples of UCu_4Pd . For instance, specific heat measurements on annealed UCu_4Pd samples show that an AF-like transition below 200 mK is suppressed toward zero temperature with increasing annealing time, thereby extending the range of NFL behavior to lower temperatures. In addition, the slope of the logarithmic divergence of γ is slightly decreased by annealing. Direct experimental evidence is still required to show whether the main effect of annealing is to change the degree of Pd/Cu site interchange, and if disorder in the U-Cu pair distance distribution is affected. This latter point is very important to quantitatively assess the observed changes in, for instance, the specific-heat data.^{8,11}

In order to further quantify the role of disorder, we report x-ray absorption fine-structure (XAFS) experiments on samples of UCu_4Pd at the Pd K and the U L_{III} edges as a function of temperature and annealing time. We find that annealing affects the site interchange (defined as the fraction, s , of the total number of Pd atoms to those sitting on $16e$ sites) and causes a slight ordering of the U-Cu pairs, demonstrating that these pairs do exhibit some static bond-length disorder, albeit very little. We consider these results in terms of various possible models.

The UCu_4Pd samples are the same as those reported in Ref. 14 with the addition of one sample that was only annealed for one day. We will not discuss the splat-cooled sample. In particular, C/T becomes constant below 180 mK in unannealed samples due to a possible AF transition,² and the Sommerfeld coefficient diverges logarithmically [$\gamma \propto \ln(T)$] above this temperature. Annealing in an evacuated quartz tube at 750°C lowers the transition temperature and the slope of the logarithmic divergence as a function of annealing time. The transition is not observed above 35 mK after 14 days of annealing. Please see Ref. 14 for further details.

The UCu_4Pd samples were prepared for the x-ray absorption measurements as described in Ref. 11. Samples were loaded into a LHe-flow cryostat, and absorption measure-

ments were collected in transmission mode on the wiggler BL 11-2 experimental station at the Stanford Synchrotron Radiation Laboratory (SSRL), using a LN₂-cooled, half-tuned double crystal monochromator. The vertical collimating slits were set to 0.7 mm for the U-edge data and 0.3 mm for the Pd-edge data. Pd-edge data were collected at $T = 20$ K and 300 K, although the 300 K data were only used to verify the low-temperature results. U-edge data were collected at 20, 100, 200, and 300 K. Two scans were collected at each temperature.

The XAFS data were reduced and fit in r space as described in Ref. 11. In particular, the XAFS oscillations are defined as $\chi(k) = \mu(k)/\mu_0(k) - 1$, where k is the photoelectron wave vector given by $\hbar^2 k^2/2m_e = E - E_0$, E is the incident photon energy, E_0 is the photoelectron threshold energy as determined by the edge position, m_e is the bare electron mass, $\mu(k)$ is the k -dependent absorption coefficient, and μ_0 is a slowly varying background that passes through the XAFS oscillations. We determine μ_0 by fitting a five-knot cubic spline (for the Pd data) or a sixth-order Chebychev polynomial (for the U data) through the XAFS above the absorption edge. The uncertainties in the present data are similar to the higher quality data in Ref. 11.

Fourier transforms of $\chi(k)$ produce peaks that, apart from a calculable phase shift, correspond to distances between the absorbing atomic species and its near neighbors. Fits provide these pair distances, r_i , as well as the pair-distance distribution widths, σ_i , for a given shell of atoms, i . Errors on the fit parameters are estimated from the differences between scans, a Monte Carlo method,¹⁵ and by comparisons to reference materials.¹⁶ These fits assume a site-interchange model¹¹ whereby s and the amplitude reduction factor S_0^2 (an overall XAFS scale factor) determine the amplitudes of all the scattering shells. Disorder apart from site interchange is accounted for only in the measurements of the various σ 's. The possible presence of such disorder is tested by fitting the U-Cu σ 's to a correlated-Debye model,¹⁷ where any observed offset σ_{static}^2 necessary between the model and the data is interpreted as static disorder. No such disorder was previously observed in the UCu_{5-x}Pd_x system within 0.0004 Å².¹¹ In order to extract the U-Cu pair σ and σ_{static} for each sample, s needs to be determined and held fixed for all the temperature data. Since determining s from the Pd-edge fits is less dependent on the fitting model (new peaks appear in the XAFS spectrum), we use the fits to the Pd data to fix s in the U fits. Values for s are only allowed to vary in the U fits as a consistency check.

Fourier transform amplitudes of $k^3\chi(k)$ for data collected at 20 K for each sample are shown in Fig. 1. The largest effects occur in the Pd data. Here, the overall amplitude increases after the first day of annealing, *except* in the region near 2.2 Å in the transform. This region has the contribution from the Pd'-Cu pairs with $r \approx 2.5$ Å, where "Pd'" denotes a Pd on the nominally Cu 16e site. The next peak is mostly due to the nominal Pd-Cu pairs with $r \approx 2.9$ Å. In fact, most of the rest of the spectrum is due to scattering that occurs in the nominal structure. Without performing any fits, these data are explained with the following argument: After an-

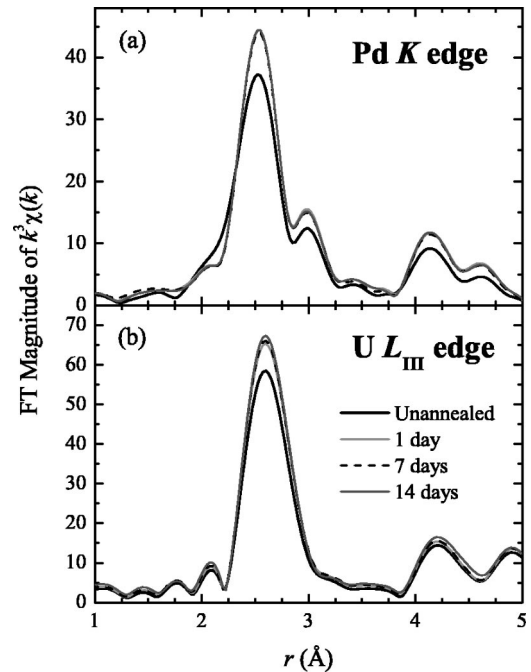


FIG. 1. Fourier transform amplitudes of $k^3\chi(k)$ XAFS data from the (a) Pd K edge and (b) the U L_{III} edge. Transform ranges are from (a) 2.5–14.8 Å⁻¹ and (b) 2.5–15 Å⁻¹, each Gaussian narrowed by 0.3 Å⁻¹.

nealing, some of the site interchanged Pd' atoms move onto the 4c sites. This rearrangement removes weight in the 2.2 Å region of the spectrum due to the relative decrease in the number of Pd'-Cu pairs, while increasing the relative number of pairs involving Pd atoms on 4c sites, thereby increasing the amplitude of the rest of the spectrum. It is important to note that no measurable changes in the spectra occur beyond the first day of annealing.

The U-edge data tell a similar story. Here, the main difference between the spectra occurs in the main XAFS peak, primarily due to U-Cu/Pd' scattering at ~ 2.9 Å. Within this same site-interchange picture, these differences are due to U-Pd' pairs converting to U-Cu pairs on annealing. The peaks beyond the main peak do not change much because for each U-Cu/Pd' pair at a given distance, there is a U-Pd pair at a very similar distance. A very important difference when comparing to the Pd edge data is that changes are observed beyond the first day of annealing, which, given the Pd edge data, cannot be easily attributed to changes in s .

Fits were performed as described above. In particular, an S_0^2 of 0.79(3) was determined for the Pd-edge fits, and 0.91(3) for the U-edge fits. These values are somewhat different than those in Ref. 11, probably due to differences in the experimental conditions. In any case, apart from the derived site interchange values reported below and pair-width parameters of some further peaks, the fit results agree very well with those reported previously, and so we refer the reader to Tables II and IV in Ref. 11.

An important source of systematic error in determining s from the Pd-edge data is the correlation between the nominal Pd-Cu pairs' distribution width σ and the measured s . This

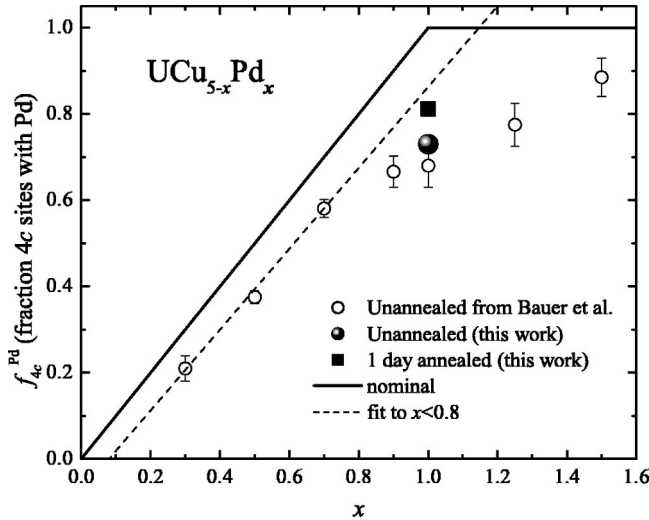


FIG. 2. The fraction of $4c$ sites occupied by Pd as a function of x in $\text{UCu}_{5-x}\text{Pd}_x$. Data from Bauer *et al.* (Ref. 11) are shown for comparison. Data for anneals longer than one day are indistinguishable on this scale.

correlation contributes to an estimated absolute error on s of about 20%. However, by holding this width fixed for all the samples, we obtain a much smaller error for comparing the differences between the data sets of $\leq 2\%$. We therefore measure $s=0.27(4)$ for the unannealed sample and $\Delta s = -0.082(7)$ after and beyond one day of annealing.

Temperature dependent fits to the U-edge data were analyzed using the correlated-Debye model. All fits can be described with a correlated-Debye temperature of $\Theta_{\text{cD}} = 314(4)$ K and $\sigma_{\text{static}}^2 = 0.0002(3) \text{ \AA}^2$, indicating little if any static disorder. Although this model describes the data well, a systematic decrease in the U-Cu pair width with annealing time is observed which can only be due to changes in a finite σ_{static}^2 . Using the data collected at 20 K, and defining $\Delta\sigma_X^2 = \sigma_{\text{U-Cu}}^2(X) - \sigma_{\text{U-Cu}}^2(14 \text{ days})$, we measure $\Delta\sigma_{7 \text{ days}}^2 = 0.00014(5) \text{ \AA}^2$, $\Delta\sigma_{1 \text{ day}}^2 = 0.00029(3) \text{ \AA}^2$, and $\Delta\sigma_{0 \text{ day}}^2 = 0.00044(4) \text{ \AA}^2$. These results are, therefore, lower limits on the static disorder in these samples. Note that a changing Θ_{cD} cannot explain this ordering, since $\sigma^2 \propto 1/\Theta_{\text{cD}}$ and the 4 K estimated error on Θ_{cD} implies a change of only about 0.00003 \AA^2 .

Two important results of the above analysis are that annealing the UCu_4Pd samples reduces the site interchange by about 30%, and that even in the sample that was annealed for 14 days, a significant amount of site interchange still occurs ($s \approx 0.19$). This latter result can be inferred from the behavior of s with changing x in $\text{UCu}_{5-x}\text{Pd}_x$.¹¹ Here we follow Weber *et al.*,¹⁴ who noted that as x increases at low x , a_0 changes linearly until $x \approx 0.85$, at which time the slope increases. The difference between the extrapolated line from low x and the measured a at $x=1$ is about 0.006 \AA . After annealing the sample, a_0 essentially agrees with the extrapolation. Bauer *et al.*¹¹ noted that the fraction of $4c$ sites occupied by Pd atoms, $f_{4c}^{\text{Pd}} = x(1-s)$, shows very similar behavior to the lattice parameter. To further these comparisons, we show a similar extrapolation (Fig. 2) using the data from

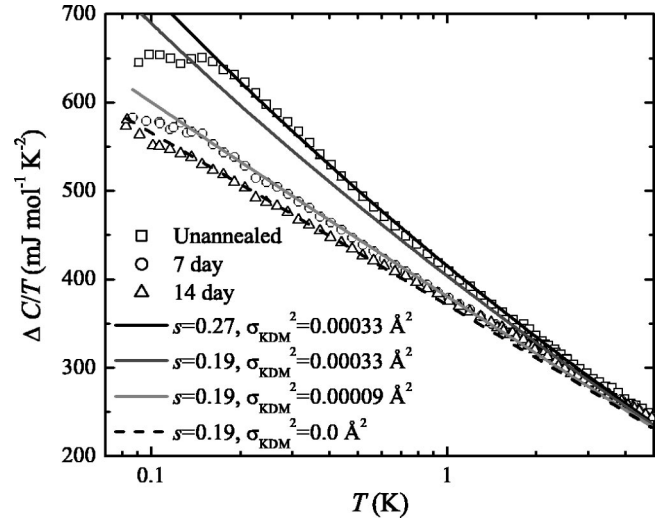


FIG. 3. The electronic part of the specific heat $\Delta C/T$ as a function of temperature from Weber *et al.* (Ref. 14) Fits are with a Kondo disorder model within a tight-binding prescription, as described in the text.

Bauer *et al.*,¹¹ together with the data collected for the present study. As in the case of the lattice parameter, the f_{4c}^{Pd} of the annealed sample agrees well with the extrapolation for $x < 0.8$.

We will now try to interpret the above results within the framework of a modified KDM and then within a generic QCP scenario. Let us first look at the KDM. The specific heat measurements (Fig. 3) show that the slope of the logarithmic divergence decreases with annealing time.¹⁴ Qualitatively, this reduction is expected from a KDM, since the reduced lattice disorder should sharpen $P(T_K)$, producing fewer low- T_K moments and therefore a slower divergence. This effect can be calculated using the same tight-binding approach as in Refs. 8,11. However, we reiterate that this model only fits the susceptibility and specific heat data if one allows a wide, static distribution of U-Cu pair distances, which is not observed in these materials.¹¹ Therefore, we are forced to assume that a large contribution to the width of $P(T_K)$ is due to some other unknown source. To describe this situation, consider a width W_V to the f /conduction electron hybridization energy distribution $P(V_{fc})$ [which generates $P(T_K)$] as arising from two uncorrelated contributions,

$$W_V^2 = W_0^2 + W_{\text{KDM}}^2,$$

where W_0 has an unidentified origin and W_{KDM} is given by a tight-binding model with the U-Cu static bond-length distribution width σ_{KDM}^2 and *no adjustable parameters* (see Ref. 11 for details). Using this distribution in a KDM, one can fit the specific-heat data allowing the Fermi energy, E_F , the ratio of the density of states at the Fermi level to the bare f -level energy, ρ/ϵ_f , and W_V to vary while holding s at the measured value, as shown in Fig. 3. Fits to the data from each of the samples allow a single set of most of these variables to be used: $E_F = 1.11 \text{ eV}$, $\rho/\epsilon_f = 0.132 \text{ eV}^{-2}$, and $W_0 = 0.1448 \text{ eV}$, where W_0 is obtained by defining $\sigma_{\text{KDM}}^2(14 \text{ days}) = 0$. These fits then give $\sigma_{\text{KDM}}^2(7 \text{ days})$

$=0.00009(3) \text{ \AA}^2$ and $\sigma_{\text{KDM}}^2(0 \text{ day})=0.00033(3) \text{ \AA}^2$, in reasonable agreement with the XAFS results. We therefore conclude that the KDM requires a significant unidentified disorder component that is not understood purely in terms of the crystal structure, but that the model can be used to describe the *changes* in the specific heat very well in terms of the measured structural changes. A possible origin of W_0 is fluctuations in the local density of states,²¹ which are not included in the present model. In any case, please note that we do not regard W_0 as necessarily describing a real width in $P(V_{fc})$, but rather that this model describes a real contribution (W_{KDM}) to the distribution width in addition to some other mechanism. The other mechanism may only be phenomenologically described in terms of a finite W_0 .

Another theoretical framework for understanding the NFL behavior is a quantum critical scenario. Here one interprets the specific-heat data in Fig. 3 as a suppression of an AF transition $T_N \rightarrow 0$ due to annealing indicated by the shift in the leveling off of the curves. The logarithmic behavior in C/T is then a consequence of quantum critical fluctuations. However, this interpretation suffers from the current lack of an established theoretical understanding how AF quantum critical fluctuations can lead to logarithmic behavior in C/T in a three-dimensional compound, though various theories have been put forward.^{18,19} Finally, we would like to note in passing that the total entropy quenched by the logarithmic slope in UCu_4Pd is consistent with the data in conventional AF transitions.²⁰

To conclude, we report measurements of the local lattice disorder as a function of annealing time in UCu_4Pd . The

XAFS measurements show that the main effect of annealing is to decrease the fraction of Pd atoms on the nominally Cu 16e sites, in agreement with the change in lattice parameter.¹⁴ Although the local U-Cu environment is well ordered, even in the unannealed samples, we observe a small but statistically significant narrowing of its pair-distance distribution on annealing. This leads to the conclusion that disorder must be included in any complete microscopic theory of NFL properties in the $\text{UCu}_{5-x}\text{Pd}_x$ system. Still, in order to quantitatively understand the NFL behavior within a Kondo disorder model, one is forced to assume a significant amount of hidden disorder. Alternatively, quantum critical fluctuations may play a dominant role for the observed NFL behavior. Alternate models that *combine* both the QCP and disorder ideas,^{12,13} might be able to fill this gap. Clearly, more work is required to arrive at a satisfactory theoretical description of the $\text{UCu}_{5-x}\text{Pd}_x$ system.

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