Copper NMR and Thermodynamics of $UCu_{5-x}Pd_x$: Evidence for Kondo Disorder

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Strong inhomogeneous broadening of the copper NMR line in $UCu_{5-x}Pd_x$, $x = 1.0$ and 1.5, indicates that spin susceptibility disorder contributes to the non-Fermi-liquid behavior of these alloys. A simple phenomenological model with a distribution of Kondo temperatures fits the field and the temperature dependence of the susceptibility, and then describes the copper NMR linewidth semiquantitatively with no further adjustable parameters. The temperature and the field dependence of the specific heat also agree well with the model.

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Certain nonmagnetic nonsuperconducting strongly correlated electron systems do not behave as Fermi liquids at low temperatures [1–3]. Anomalous properties were first identified in the Kondo alloy $Y_{0.8}U_{0.2}Pd_3$ [2], and similar behavior was discovered in $UCu_{5-x}Pd_x$, $1.0 \leq x \leq 1.5$ [3]. Among the non-Fermi-liquid anomalies observed at low temperatures were a linear temperature dependence of the resistivity and lack of saturation of both the magnetic susceptibility $\chi(T)$ and the linear temperature coefficient $C(T)/T$ of the specific heat. The origin of these phenomena has been the subject of considerable controversy.

This Letter reports a study of magnetization and Cu nuclear magnetic resonance (NMR) in the Kondo alloys $UCu_{5-x}Pd_x$, $x = 1.0$ and 1.5, and their interpretation in the context of non-Fermi-liquid behavior. For both Pd concentrations we observe a large and strongly temperature-dependent inhomogeneous NMR linewidth, reflecting a broad distribution of local U-spin static susceptibilities. We were led to consider a simple model of "Kondo disorder," which attributes the susceptibility inhomogeneity to a distribution $P(T_K)$ of Kondo temperatures T_K. Parameters characterizing $P(T_K)$ were extracted from fits to the uniform magnetic susceptibility $\chi(H,T) \equiv M(H,T)/H$, now thought of as the average of $\chi(H,T;T_K)$ over $P(T_K)$. Then the NMR linewidths, which are due to the distribution of Knight shifts and measure directly the width of the distribution $P(\chi)$ of χ, are found to agree well with the model without any further fitting of $P(T_K)$, as are the temperature and the field dependence of the specific heat. These results demonstrate unambiguously that disorder plays an important role in the non-Fermi-liquid behavior of $UCu_{5-x}Pd_x$.

Before describing our NMR experiments in UCu_4Pd and $UCu_{3.5}Pd_{1.5}$ in detail, we define our Kondo-disorder model and fit it to the temperature and the field dependence of the magnetic susceptibility. We then compare the model's predictions with the measured NMR linewidth and specific heat.

The Kondo coupling constant $\lambda = \rho|J|$, where ρ is the density of conduction-electron states at the local-moment site and J is the conduction-electron–local-moment exchange coupling, determines T_K and its distribution. Separate theories of disorder in J [4] and ρ [5] have been reported, the latter in terms of a disorder parameter u and only valid for the case of strong disorder ($u > 1$). In $UCu_{3.5}Pd_{1.5}$ both $\chi(T)$ and $C(T)/T$ are seen to increase slowly rather than diverge rapidly as the temperature is lowered [3]. This suggests that the disorder is weak, and preliminary attempts to fit the theory of Ref. [5] to the $\chi(T)$ data indeed resulted in values of $u \sim 0.01$, a clear violation of the condition $u > 1$.

We therefore assume that the distribution of Kondo temperatures arises from a relatively narrow Gaussian distribution $P(\lambda)$, with average $\langle\lambda\rangle$ and rms width w [6]. We take $T_K(\lambda) = \varepsilon_F \exp(-1/\lambda)$, where ε_F is the Fermi energy, and find the probability distribution $P(T_K) = |d\lambda/dT_K|P(\lambda)$. Such a disordered Kondo system will deviate from Fermi-liquid behavior at low temperatures if a significant number of Kondo impurities possess low Kondo temperatures, i.e., behave as nearly free magnetic moments [4,5]. Crudely speaking, the thermodynamics of the system at temperature T will be dominated by those Kondo impurities for which $T_K < T$.

Knowledge of $P(T_K)$ allows one to calculate the average and all other moments of the susceptibility:

$$\langle\chi^n(H,T)\rangle = \int_0^\infty dT_K\, P(T_K)\, \chi^n(H,T;T_K). \quad (1)$$

We set $\chi(H,T;T_K) = g\mu_B J B_J(x)/H$, where g is the Landé g factor, J is the effective angular momentum of the U ions, and $B_J(x)$ is the Brillouin function. Single-ion Kondo physics is included by defining $x \equiv g\mu_B JH/k_B(T + \alpha T_K)$, $\alpha = \sqrt{2}$ [7]. Although more up-to-date scalings of Kondo-system thermodynamics are available [8], the replacement $T \rightarrow T + \alpha T_K$ successfully models NMR and susceptibility measurements in a number of conventional Kondo systems [9]. We have used it here for simplicity and to minimize the number of parameters.

Figure 1 displays $\chi(H,T)$ for temperatures from 1.8 to 400 K at fields of 5 and 50 kOe, together with fits to

the mean $\langle\chi\rangle$ from the model [Eq. (1) with $n = 1$]. The numerical values of the fit parameters are summarized in Table I. The good accuracy of these parameters, particularly w, is mainly due to the field dependence of χ at low temperatures, which arises in the model from the saturation of nearly free low-T_K moments. This does not occur if T_K is uniform ($w = 0$), in which case $\chi(T)$ is field independent below 50 kOe and much smaller (dashed curves in Fig. 1). We find similar values of $\langle\lambda\rangle$ and $w \simeq 0.18\langle\lambda\rangle$ for both concentrations. [The rms width of $P(T_K)$ is of course much greater; $(\delta T_K)_{\rm rms} \sim \langle T_K\rangle$.] This similarity is qualitatively consistent with the NMR linewidth (see below) and quasielastic neutron scattering spectra [10], neither of which depends strongly on Pd concentration. The fit values of the effective Bohr magneton number $p \equiv g\sqrt{J(J+1)}$ agree with those found from the asymptotic behavior of χ at high temperatures [3,11]. The average Kondo temperature $\langle T_K\rangle$ is lower for $UCu_{3.5}Pd_{1.5}$ than for UCu_4Pd, also in agreement with the high-T behavior of χ.

The goodness of these fits is consistent with, but not particularly strong evidence for, Kondo disorder. The rapidly varying and large NMR linewidth, which we argue arises directly from a broad susceptibility distribution, is more compelling. In the following we describe our NMR experiments and their analysis.

Figure 2 shows typical Cu NMR field-swept powder pattern spectra for UCu_4Pd and $UCu_{3.5}Pd_{1.5}$. The two large peaks are the $(1/2 \leftrightarrow -1/2)$ central transitions of ^{65}Cu and ^{63}Cu isotopes, as indicated in the figure. The first-order quadrupolar satellites are resolved in the UCu_4Pd spectra, but are strongly broadened in $UCu_{3.5}Pd_{1.5}$. The central transitions are about equally broadened in both alloys, which indicates that the satellite broadening is quadrupolar and due to greater charge disorder in $UCu_{3.5}Pd_{1.5}$. For $x < 2.3$ $UCu_{1-x}Pd_x$ crystallizes in the $F\bar{4}3m$ space group, with sites of $\bar{4}3m$ (tetrahedral) and $3m$ (trigonal) point symmetry in the ratio 1:4 occupied by the Cu and Pd atoms. NMR spectra from Cu atoms at $\bar{4}3m$ sites would not be quadrupole split, and the absence of unsplit lines in the observed spectra is consistent with preferential occupation of the $\bar{4}3m$ site by Pd atoms [3].

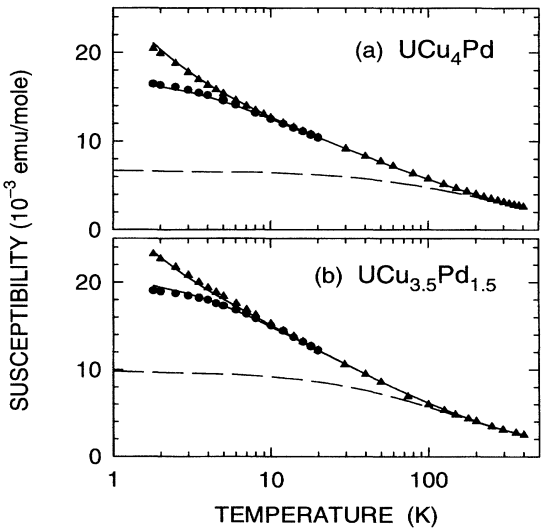

FIG. 1. Temperature dependence of the magnetic susceptibility of (a) UCu_4Pd and (b) $UCu_{3.5}Pd_{1.5}$ at $H = 5$ kOe (triangles) and 50 kOe (circles). Solid curves: fits to $\langle\chi\rangle$ from Eq. (1) ($n = 1$), with parameters given in Table I. Dashed curves: uniform Kondo model ($w = 0$).

The curves in Fig. 2 are fits to second-order calculations of axially symmetric quadrupole-split powder patterns [12] convolved with symmetric broadening functions. To second order in the quadrupolar splitting magnetic contributions to the shift and broadening of the central transition are proportional to the Zeeman frequency ν_0, whereas quadrupolar contributions are inversely proportional to ν_0 [12]. Using this frequency dependence, we extracted the raw isotropic Knight shift $K_{\rm iso}^{\rm raw}$, the axial anisotropic Knight shift $K_{\rm ax}$, and the rms width $(\delta H)_{\rm rms}$ of the central transition Gaussian broadening function. In both alloys the inverse of the measured spin-echo lifetime $T_2 \sim 250\,\mu$s is much smaller than $(\delta H)_{\rm rms}$ in frequency units, so that lifetime broadening is negligible and $(\delta H)_{\rm rms}$ can only be due to static disorder. For $T \gtrsim 30$ K, $K_{\rm iso}^{\rm raw}(\chi)$, with temperature an implicit parameter, is linear in both samples, yielding [12] an average effective field $H_{\rm eff} = N\mu_B(dK_{\rm iso}/d\chi) = -3.3 \pm 0.2$ kOe/μ_B. The zero-χ intercept was interpreted as the non-heavy-fermion conduction-electron Knight shift, and was subtracted from $K_{\rm iso}^{\rm raw}$ to yield the heavy-fermion contribution $K_{\rm iso}$. For both samples $K_{\rm ax}$ was proportional to $K_{\rm iso}$, and will not be discussed further.

The local Knight shift $K(\mathbf{r})$ can be written $K(\mathbf{r}) = a(\mathbf{r})\chi(\mathbf{r})$, where the hyperfine coupling $a(\mathbf{r})$ and the local susceptibility $\chi(\mathbf{r})$ are both spatially nonuniform. If their distributions are uncorrelated the distribution average $\langle K\rangle = \langle a\chi\rangle = \langle a\rangle\langle\chi\rangle$. Similarly, the fractional NMR linewidth $\kappa \equiv (\delta H)_{\rm rms}/H$ is given by

$$\kappa = (\delta K)_{\rm rms} = [\delta(a\chi)]_{\rm rms},$$

so that for uncorrelated a and χ

$$\frac{\kappa}{|\langle K\rangle|} \approx \sqrt{\left(\frac{(\delta\chi)_{\rm rms}}{\langle\chi\rangle}\right)^2 + \left(\frac{(\delta a)_{\rm rms}}{\langle a\rangle}\right)^2}. \qquad (2)$$

TABLE I. Parameters for fits of the susceptibility to the Kondo-disorder model in $UCu_{5-x}Pd_x$, $x = 1.0$ and 1.5. See text for symbols.

Parameter	UCu_4Pd	$UCu_{3.5}Pd_{1.5}$
$\langle\lambda\rangle$	0.21 ± 0.01	0.22 ± 0.01
$\langle T_K\rangle$ (K)	173 ± 5	95 ± 4
w	0.040 ± 0.001	0.041 ± 0.001
p	3.63 ± 0.20	3.26 ± 0.03
J	3/2 (fixed for both alloys)	

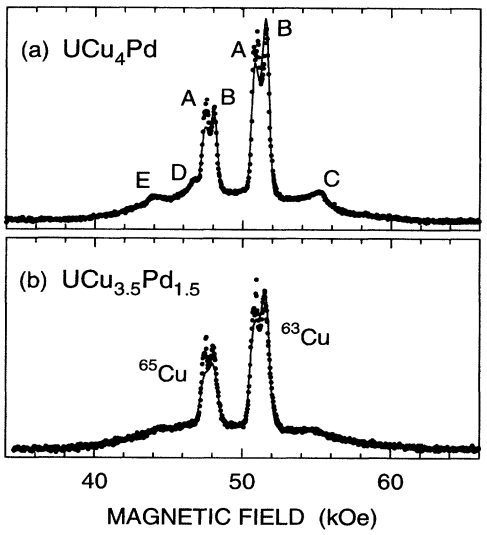

FIG. 2. Representative Cu NMR spectra from (a) UCu_4Pd and (b) $UCu_{3.5}Pd_{1.5}$, $T = 120$ K, spectrometer frequency $\nu_0 = 57.6$ MHz. Points: NMR data. Curves: fits to broadened quadrupole-split powder patterns with anisotropic Knight shifts. The best-fit broadening functions are Gaussian for the central transitions and Lorentzian for the satellites. The large peaks are central transitions for ^{63}Cu and ^{65}Cu isotopes. *A, B*: powder-pattern singularities in central transitions. *C, D*: ^{63}Cu ($3/2 \leftrightarrow 1/2$) quadrupole satellites. *E*: ^{65}Cu ($3/2 \leftrightarrow 1/2$) quadrupole satellite. The small extra lines are due to *Cu*Pd impurity phases.

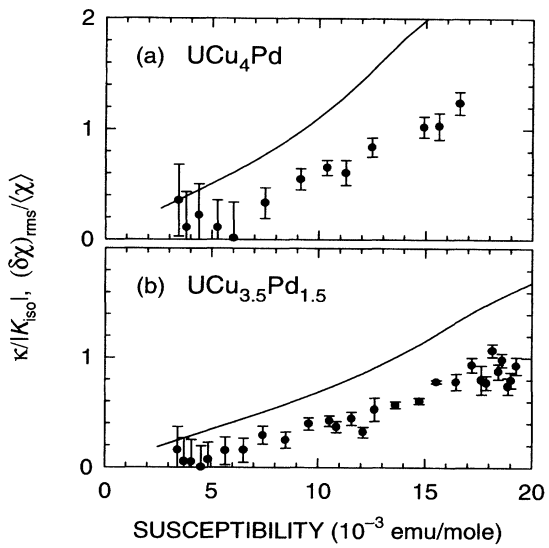

FIG. 3. Dependence of relative distribution widths on magnetic susceptibility, with temperature an implicit parameter, in (a) UCu_4Pd and (b) $UCu_{3.5}Pd_{1.5}$. Data points: measured relative NMR linewidths $\kappa/|K_{iso}|$. Curves: numerical calculations of the relative width $(\delta\chi)_{rms}/\langle\chi\rangle$ using the Kondo-disorder model described in the text.

Thus $\kappa/|\langle K\rangle|$ varies with $\langle\chi\rangle$ unless $(\delta\chi)_{rms}$ vanishes or is proportional to $\langle\chi\rangle$. A heuristic picture for $\kappa(\chi)$ in the Kondo-disorder model is the following: assume χ follows a Curie-Weiss law $\chi \propto 1/(T + \alpha T_K)$. If T_K is distributed, then $(\delta\chi)_{rms} \approx |\partial\langle\chi\rangle/\partial T_K|(\delta T_K)_{rms}$, i.e., $(\delta\chi)_{rms} \propto \langle\chi\rangle^2$ for fixed $(\delta T_K)_{rms}$, and $\kappa/|\langle K\rangle|$ is proportional to $\langle\chi\rangle$ if $(\delta a)_{rms}$ does not contribute significantly.

We therefore display the Cu NMR linewidths in Fig. 3 as the dimensionless parameter $\kappa/|K_{iso}|$ vs $\langle\chi\rangle$. The data of Fig. 3 show no sign of a nonzero constant term [Eq. (2)], and suggest that the dependence of $\kappa/|K_{iso}|$ on $\langle\chi\rangle$ is at least linear and may be faster. We conclude that the NMR linewidth is dominated by distribution of the magnetization rather than the hyperfine field.

There are two striking aspects of these data. The first is that $\kappa/|K_{iso}|$ is rapidly varying and large (of order unity) at large χ. This indicates strong magnetic disorder; an ordered compound would exhibit a Knight shift but no inhomogeneous NMR broadening. The increase of $\kappa/|K_{iso}|$ at low temperatures (large χ) for both concentrations could suggest the presence of contributions to the linewidth from antiferromagnetic or disordered spin freezing [13], which might not modify the bulk magnetization strongly but would affect the local magnetic environment probed by NMR. The field dependence of the NMR linewidth in $UCu_{3.5}Pd_{1.5}$ [14] and UCu_4Pd [15] indicates, however, that its enhancement is not likely to arise from static magnetic moments.

The second surprising aspect is that $\kappa/|K_{iso}|$ behaves very similarly for both samples. It is not hard to understand disorder in $UCu_{3.5}Pd_{1.5}$, since Pd ions occupy the $3m$ sites randomly in this alloy, but x-ray diffraction [3] suggests that UCu_4Pd is an ordered compound. This must not be entirely the case, since the NMR broadening is an unambiguous indicator of magnetic disorder.

A crucial test of the Kondo-disorder model is comparison of its prediction for $(\delta\chi)_{rms}/\langle\chi\rangle$ with the observed $\kappa/|K_{iso}|$; for negligible $(\delta a)_{rms}/\langle a\rangle$ these two quantities should be equal [Eq. (2)]. Figure 3 gives the calculated $(\delta\chi)_{rms}/\langle\chi\rangle$ for both concentrations, using the parameters of Table I with no further adjustment. The rough agreement, which is the central result of this paper, shows that the model accounts semiquantitatively for the NMR linewidth. Possible sources of the factor-of-2 disagreement include (1) inadequate representation of the Kondo magnetization by a single-impurity theory and the simple replacement $T \rightarrow T + \alpha T_K$ in the free-spin Brillouin function; (2) second-phase impurity-spin contributions to the measured $\chi(H, T)$, which would make the fit to the model $\langle\chi(H, T)\rangle$ overestimate the distribution widths; and (3) underestimation of the experimental value of κ because the broadening is taken to be Gaussian; the model broadening function $P(\chi)$ is asymmetric, with a larger second moment than the best-fit Gaussian. In light of these caveats better agreement cannot be expected, and improvements of the model would be futile until the importance of point (2) above can be assessed. It is nevertheless clear that the magnitude of the NMR linewidth and its dependence on $\langle\chi\rangle$ are accounted for by the Kondo-disorder model.

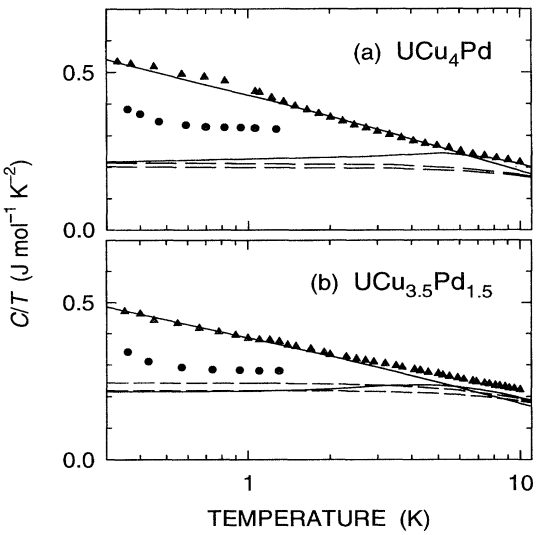

FIG. 4. Temperature dependence of specific heat coefficient $C(T)/T$ of (a) UCu_4Pd and (b) $UCu_{3.5}Pd_{1.5}$ at $H = 0$ (triangles, upper curves) and 140 kOe (circles, lower curves) [3]. Solid curves: Kondo-disorder model, with Kondo specific heat from resonant-level model [16]. $H = 0$ and 140 kOe. Dashed curves: uniform Kondo model.

Figure 4 displays specific heat data for UCu_4Pd and $UCu_{3.5}Pd_{1.5}$ over the temperature range 0.3–10 K, $H = 0$ and 140 kOe [3]. The solid curves give the Kondo-disorder model average of $C(H,T;\Delta)/T$ over $P(T_K)$, where $C(H,T;\Delta)$ is the resonant-level model specific heat for a single Kondo impurity [16]. Here $\Delta \propto T_K$ is the width of the resonance; for best fit to the zero-field data the average $\langle\Delta\rangle$ is close to 55 K for both concentrations. The other parameters are again taken from Table I without further adjustment, and again we obtain rough agreement. The zero-field upturn and field dependence at low temperatures are due to the low-T_K free spins; the field displaces the free-spin Schottky anomalies to higher temperatures, thus reducing the low-temperature specific heat. As for the susceptibility, the size and field dependence of the low-temperature specific heat are much smaller in the uniform Kondo model (dashed curves in Fig. 4).

We conclude that Kondo disorder is a dominant feature of non-Fermi-liquid behavior in $UCu_{5-x}Pd_x$. The susceptibility of these alloys is strongly affected by Kondo disorder, and comparisons of χ with other properties must be reconsidered in light of this feature. It would be premature, however, to conclude that all the non-Fermi-liquid properties of $UCu_{5-x}Pd_x$ are due to Kondo disorder, which is certainly not the only possible origin of non-Fermi-liquid behavior. NMR and muon spin rotation studies of these and other non-Fermi-liquid metals are currently in progress.

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