NMR evidence for Kondo disorder in $UCu_{3.5}Pd_{1.5}$

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We report on Cu nuclear quadrupole resonance (NQR) and nuclear magnetic resonance experiments probing the cubic non-Fermi-liquid compound $UCu_{3.5}Pd_{1.5}$. The NQR spectrum indicates a partial disorder in the occupation of Cu and Pd sites, with a preferential occupation of the cubic *c* site by Pd. Our results for the temperature dependence of the nuclear magnetization recovery show unusual features that cannot be reconciled with common expectations for a simple metal, but they are well accounted for in a description using the Kondo disorder model. [S0163-1829(99)50740-6]

Recently the low-temperature thermal and transport properties of a number of paramagnetic *f*-electron alloys have been found to not be compatible with a simple Landau Fermi-liquid behavior,[1,2] among them the alloy series $UCu_{5-x}Pd_x$ for $1 \leqslant x \leqslant 1.5$.[3] In particular, studies of $UCu_{3.5}Pd_{1.5}$ have initiated the proposal of the so-called Kondo disorder model (KDM),[4,5] which considers a broad distribution of Kondo temperatures as the origin for the divergence of its properties from Fermi-liquid behavior.[6,7] Disorder is an issue here, because $UCu_{5-x}Pd_x$ with $0 \leqslant x \leqslant 2.3$ crystallizes in the fcc $AuBe_5$-type structure. The uranium ions occupy the four *a* sites (in Wyckoff notation) with $\overline{4}3m$ symmetry and the Cu (or Pd) atoms are on two crystallographically inequivalent sites, the four *c* sites with $\overline{4}3m$ symmetry and the 16 *e* sites with only $3m$ symmetry. In the parent compound UCu_5 only the *e* sites experience a non-zero electric-field gradient.

Very recently a debate has developed questioning the relevance of the KDM model for the $UCu_{5-x}Pd_x$ series of alloys.[8,9] Based on the results of elastic neutron-diffraction measurements, it has been claimed that UCu_4Pd is a chemically ordered compound with 100% Pd atoms occupying the four *c* sites.[8] The results presented in Ref. [9], however, suggest that lattice disorder is indeed at the origin of the non-Fermi-liquid behavior of UCu_4Pd.

In this work we present convincing experimental evidence for chemical disorder in $UCu_{3.5}Pd_{1.5}$ and argue that the KDM is very well suited for describing the anomalous Cu nuclear magnetic relaxation in this compound. Our results for the nuclear quadrupole resonance (NQR)/nuclear magnetic resonance (NMR) spectra of $UCu_{3.5}Pd_{1.5}$ indicate a distinct degree of disorder in the occupation of both the *c* and the *e* sites by Pd and Cu, respectively, and the temperature dependence of the spin-lattice relaxation provides strong support that the KDM applies for $UCu_{3.5}Pd_{1.5}$. Small deviations from the expectations of this model are observed at low fields and at temperatures below 2 K.

The $UCu_{3.5}Pd_{1.5}$ material used in our NMR investigation was prepared by arc melting suitable amounts of U, Cu, and Pd in an argon atmosphere. The corresponding $AuBe_5$-type crystal structure was verified by a powder x-ray diffraction pattern. Our NMR sample was prepared by powdering a piece of this polycrystalline $UCu_{3.5}Pd_{1.5}$ in an argon atmosphere to grains with a typical size of less than 100 μm. Our material is well characterized by thermal, transport, and optical properties.[10] For our experiments, we have used common spin-echo NMR techniques.[11]

In Fig. 1 we show the NQR spectrum of $UCu_{3.5}Pd_{1.5}$ measured at $T = 4.1$ K (open circles). The full circles in the same figure represent the NQR spectrum of the parent compound UCu_5 measured in the paramagnetic phase at $T = 77$ K under similar conditions. The peaks near 12 and 13 MHz in the NQR spectrum of UCu_5 correspond to the signals from both ^{65}Cu and ^{63}Cu at the Cu-*e* sites. The total width of the observed $UCu_{3.5}Pd_{1.5}$-NQR spectrum is approximately 8 MHz, centered at about $\nu = 12$ MHz, in proximity to the frequencies of the NQR lines of UCu_5. Therefore, it seems very likely that this NQR spectrum arises exclusively from Cu atoms occupying the *e* sites. The large width of the spectrum is consistent with the disorder introduced by the Pd substitution of Cu. The signal intensity arising from Cu on *c* sites is expected to be at lower frequencies, since the Cu-*c*-site en-

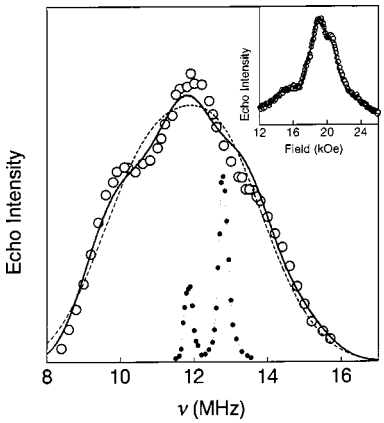

FIG. 1. Cu-NQR spectrum of $UCu_{3.5}Pd_{1.5}$ measured at 4.2 K (open circles). The full circles represent the Cu-NQR spectrum of UCu_5 measured in the paramagnetic phase at $T = 77$ K. The solid line represents the best fit to the data implying a Pd occupation of the *c* sites of 70%. The best fit for an occupation of 100% is shown by the broken line. In the inset we show an NMR spectrum of $UCu_{3.5}Pd_{1.5}$ measured at $\nu = 21.87$ MHz and $T = 0.08$ K (open circles). The solid line represents the results of our simulation of the NMR spectrum (see text).

vironment in UCu_5 has cubic symmetry. The *c* sites in the structure of $UCu_{3.5}Pd_{1.5}$ are believed to be occupied by Pd atoms by more than 70%,[8,9] which statistically leads to essentially three different nearest neighbor (n.n.) environments for the Cu atoms on the *e* site, namely, with 0, 1, and 2 Pd n.n. An environment with 3 Pd n.n. is statistically only significant for a Pd occupation of the *c* sites by less than 70% and hence this unlikely situation will not be considered any further.

For each of these three environments we assume a Gaussian distribution of quadrupole frequencies all with equal width. The center of each Gaussian is determined by the number of Pd n.n. and the relative intensities are fixed by the relative probabilities of each environment to occur, given the partial occupation of the *c* sites by Pd atoms. The best fits to the data of our four-parameter model,[12] corresponding to Pd occupations of the *c* sites of either 70% or 100%, are shown in Fig. 1 by the solid and the broken line, respectively. Although the 70%-occupation best fit shows some deviations from the data points, it reproduces the essential features of our NQR spectrum rather well. The average quadrupole frequencies $\langle \nu_Q \rangle^j$ of ^{63}Cu obtained from this fit are 13.2, 11.5, and 9.7 MHz for $j=0,1,2$ Pd n.n., respectively. The ^{63}Cu environment with only Cu n.n. has $\langle \nu_Q \rangle^0 = 13.2$ MHz, obviously very close to the observed quadrupole frequency of ^{63}Cu in UCu_5 (see Fig. 1), thus adding confidence in the reliability of our approach. The best fit to the data assuming a full occupation of *c* sites by Pd leads to a broad featureless structure (broken line in Fig. 1). Further support for our interpretation of partial disorder is obtained by comparing the results of our simulations and the NMR spectra collected at several fixed frequencies. A convincing example is shown in the inset of Fig. 1 where we display the NMR spectrum collected at a fixed frequency $\nu = 21.87$ MHz and $T = 0.08$ K (open circles). The solid line represents a powder-pattern simulation of the signal obtained by solving explicitly the full Hamiltonian and inserting the quadrupolar parameters quoted above. We note here that no free parameter other than an overall scaling factor was used. Equally excellent agreement between the simulations and the observed spectra is obtained at still higher frequencies.[13]

In addition to the NQR/NMR spectra we have measured the nuclear magnetization recovery $m(t)$ for the central transition of ^{63}Cu after the application of one or more rf pulses. Changes of the widths or the number of the applied rf pulses in the short comb were found to produce no appreciable changes in $m(t)$. Although no detailed T_1 profiles of the NMR lines were established, no drastic changes of the nuclear magnetization recovery were observed near the center of the line. This is, in fact, not surprising because the linewidth is dominated by quadrupolar effects. In Fig. 2 we show this in the form of $1-m(t)/m(\infty)$ at 5.1 T for nine different temperatures between 0.1 and 236 K (symbols). A first inspection of the data, i.e., noting the changes in the shape of $m(t)$, led to the conclusion that the usual approach for describing the relaxation with a single value of a relaxation rate T_1^{-1} is not adequate in this case. The solid lines in the same figure represent the results of our calculations for the corresponding temperatures, applying the Kondo disorder model as discussed in some details below.

For interpreting the spin-lattice relaxation in $UCu_{3.5}Pd_{1.5}$

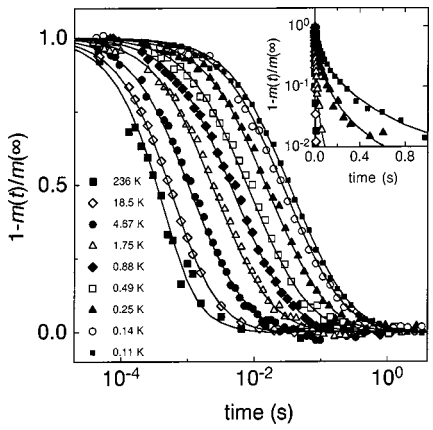

FIG. 2. ^{63}Cu-nuclear magnetization recovery in $UCu_{3.5}Pd_{1.5}$ measured at $H=5.1$ T for nine different temperatures between 0.11 K and 236 K (symbols). The solid lines represent calculations of $1-m(t)/m(\infty)$ at the respective temperatures, based on the Kondo disorder model as explained in the text. The inset shows data for five different temperatures and emphasizes the changes of the relaxation behavior at high and low temperatures.

invoking the KDM we first need the distribution of Kondo temperatures $P(T_K)$, which we obtain from the dc susceptibility data measured on our sample.[14] Following the procedure of Bernal *et al.*[4,5] we introduce the Kondo physics using the single ion susceptibility being defined as

$$\chi(H,T+\alpha T_K) = \frac{g\mu_B J B_J\left(\dfrac{g\mu_B JH}{k_B(T+\alpha T_K)}\right)}{H}, \qquad (1)$$

where all the symbols have the same meaning as in Ref.4, B_J is the Brillouin function and α is a constant of order unity. We obtain a $P(T_K)$ similar but not identical to that reported in Ref. 4. Next we consider the nuclear spin-lattice relaxation rate in the presence of a magnetic ion. If we neglect the wave-number dependence of the susceptibility, the spin-lattice relaxation rate can be expressed[15–17] as

$$\frac{1}{T_1} = 2\gamma H_{hf} k_B T \chi \frac{1}{\Gamma}, \qquad (2)$$

where γ is the gyromagnetic ratio of the Cu nuclei, H_{hf} the transferred hyperfine field at the nucleus, χ is defined in Eq. (1), and Γ denotes the correlation rate of the *f*-moment fluctuations. Following the suggestions of Cox *et al.*.[18] we take $\Gamma(T) \propto 1/\chi(T)$ at very low temperatures, and $\Gamma(T) \propto \sqrt{T/T_K}$ at high temperatures. A simple interpolation between these two limits leads to

$$\frac{1}{T_1} = C\,\chi^2(H,T+\alpha T_K)\,T \quad \text{for} \quad T \leqslant T_K, \qquad (3)$$

and

$$\frac{1}{T_1} = C\,C_{T_K}\chi(H,T+\alpha T_K)\sqrt{T} \quad \text{for} \quad T > T_K, \qquad (4)$$

where C_{T_K} is a multiplicative factor to ensure the continuity of T_1^{-1} at $T=T_K$, and C is a constant that is determined once

and for all by the ''best'' fit to the data at any given temperature and field. Experimentally a qualitative behavior similar to that given by Eqs. (3) and (4) has previously been found in *f*-electron compounds.[19,20] As a next step we consider the spin-lattice relaxation due to *all* the *f*-electron moments. For this purpose we assume that the Kondo temperature of neighboring U ions and the fluctuating field produced by different U moments at the site of a particular Cu nucleus are uncorrelated. This assumption may be considered as a simple extension of the ''short range correlation'' between neighboring Kondo centers discussed in Ref. 5. Thus the spin-lattice relaxation rate $(T_1^i)^{-1}$ at the Cu-site i can be taken as a sum over the individual U contributions

$$\frac{1}{T_1^i} = \sum_j \frac{1}{T_1^{ij}(T_K^j)} \quad , \tag{5}$$

where $1/T_1^{ij}(T_K^j)$ is the nuclear relaxation rate at the Cu-site i, induced by the U ion at the site j (with a Kondo temperature T_K^j). The transferred hyperfine field and hence $1/T_1^{ij}$ strongly depend on the distance r_{ij} between the Cu nucleus i and the U magnetic moment j. For keeping the analysis manageable we have introduced an effective number of equidistant neighbors $n_{\rm eff}$, so that the sum in Eq. (5) extends only up to $n_{\rm eff}$ terms. The best agreement between the model calculations and the measured nuclear magnetization recoveries is obtained for $n_{\rm eff}=7$, which in $UCu_{3.5}Pd_{1.5}$ corresponds to the sum of nearest and next nearest U neighbors of a given Cu *e* site and therefore this value seems reasonable. Finally, Eq. (5) is inserted in the appropriate form of the nuclear magnetization recovery

$$\begin{aligned} 1-\frac{m(t)}{m(\infty)} \propto & \int \cdots \int \left[0.9 \exp\left\{ -6t \sum_{j=1}^{n_{\rm eff}} [1/T_1(T_K^j)] \right\} \right. \\ & \left. + 0.1 \exp\left\{ -t \sum_{j=1}^{n_{\rm eff}} [1/T_1(T_K^j)] \right\} \right] \\ & \times \prod_{j=1}^{n_{\rm eff}} P(T_K^j)\, dT_K^j \\ \equiv & \int [0.9 e^{-6(t/T_1)} + 0.1 e^{-(t/T_1)}] \\ & \times D(T_1^{-1})\, dT_1^{-1}, \end{aligned} \tag{6}$$

valid for very short rf irradiation of the central line in the high-field limit, i.e., the Zeeman interaction dominates over the quadrupole interaction. The last identity of Eq. (6) simply defines the resulting distribution $D(T_1^{-1})$ of relaxation rates.

As shown in Fig. 2, the remarkable agreement between our model calculation and the experimentally monitored nuclear magnetization recovery, extending over the entire measured temperature range from 0.1 to 300 K, is a strong indication for the validity of our simple approach and gives convincing evidence that Kondo disorder plays a major role in $UCu_{3.5}Pd_{1.5}$. We emphasize that our simple model has only two free parameters, i.e., the effective number of U neighbors $n_{\rm eff}$ of a Cu *e* site and an overall prefactor C in the spin-lattice relaxation rate entering Eqs. (3) and (4).

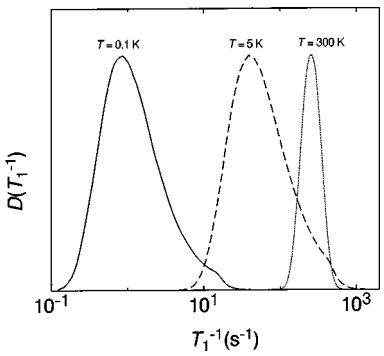

FIG. 3. Temperature dependence of the distribution of $1/T_1$ as obtained from fitting the nuclear magnetization recovery data displayed in Fig. 2.

In Fig. 3 we display $D(T_1^{-1})$ at $H=5.1$ T (data from Fig. 2) for three different temperatures between 0.1 and 300 K. At low temperatures the $D(T_1^{-1})$ is very broad as expected from the T_K^{-2} dependence of T_1^{-1} given by Eq. (3). At high T, $D(T_1^{-1})$ is much more narrow due to the weaker T_K dependence of T_1^{-1} [see Eq.(4)].

In order to test the validity of our model further, we have also used it to analyze the nuclear magnetization recovery data obtained for $H=1.93$ T, where the Zeeman and the quadrupole interactions are of comparable magnitude. In this case we have replaced the term in brackets of Eq. (6) by a numerical calculation of the nuclear magnetization recovery[21] for a powder pattern at 1.93 T ($\nu=21.87$ MHz), the field at which the recovery was monitored. The applied field also enters explicitly in our calculation via the spin-lattice relaxation rate equations (3)-(4).

We compare our calculations with the experimental data for five temperatures and $H=1.93$ Tesla in Fig. 4. At temperatures $\gtrsim 2$ K the predictions of the KDM and the experimental data are in remarkably good agreement, although no adjustable parameter has been used in this calculation. The parameters $n_{\rm eff}$ and C are the same as those used in the 5.1 T calculation. Although some deviations between experiment and calculation for temperatures below 2 K cannot be de-

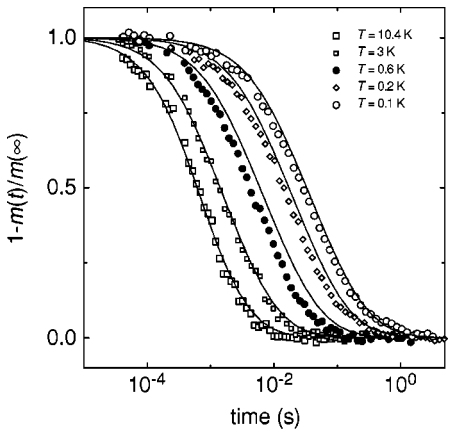

FIG. 4. Cu-nuclear magnetization recovery in $UCu_{3.5}Pd_{1.5}$ measured at $H=1.93$ T for five different temperatures. The solid lines represent the calculated $1-m(t)/m(\infty)$ at the respective temperatures assuming the parameters C and $n_{\rm eff}$ obtained from the simulations at 5.1 T (see text).

nied, the overall agreement indicates again that the observed spin-lattice relaxation is influenced by a distribution of Kondo energy scales. All our attempts to explain our data with a single value for T_K failed.

In conclusion the results of our NQR/NMR measurements provide evidence that although the Pd atoms preferentially occupy the *c* sites of the unit cell, the occupation is only of the order of 70%, confirming that chemical disorder is present on both the *c* and the *e* Cu or Pd sites. Our nuclear magnetization recovery data imply an increasing degree of relative broadening of the distribution of the spin-lattice relaxation rates with decreasing temperature. The impressive agreement between our model calculation assuming a distribution of Kondo temperatures and the experimental data for both high- and medium-field conditions give strong evidence that disorder plays an essential role for the spin-lattice relaxation in $UCu_{3.5}Pd_{1.5}$. Altogether this also suggests that disorder is at the origin of the non-Fermi liquid behavior of this alloy.

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[12] Since the parameters for one Cu isotope fully determine the parameters for the other, the model has only four free parameters: the centers of the three Gaussians and the common width. The model also assumes a random distribution of the asymmetry parameters of the field gradients.

[13] To fit the NMR spectra at much higher frequencies one has also to consider an inhomogeneous Knight shift. Details of these considerations and results will be published in Ref. 14.

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