Cu-NMR spectra in UCu$_4$Ni uncover site disorder

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Abstract. Cu-NMR measurements in a random powder of UCu$_4$Ni reveal two types of spectral lines for each of the two isotopes of naturally abundant Cu in the material. These lines, which we label $L_1$ and $L_2$, point to the existence of two inequivalent Cu sites in the sample. We present a study of the NMR line shape in UCu$_4$Ni at three different frequencies (in the range from 40-70 MHz) and two temperature values (10 K and 150 K), that allow us to assign the lines to particular Cu sites. $L_1$ is strongly broadened as the frequency decreases, but changes less with increasing temperature. In contrast, the width of $L_2$ grows in proportion to frequency and decreases noticeably with increasing temperature. This behavior indicates that the crystallographic site corresponding to $L_1$ is exposed to electric field gradients and has lower point symmetry than the site corresponding to $L_2$, which displays some anisotropy but no discernible quadrupole effects. By comparison with the Cu-NMR spectra in UCu$_4$Pd, where only one type of Cu-NMR line has been observed clearly, we can associate $L_1$ with Cu$^{(16e)}$ nuclei: Cu nuclei sitting at the 16e site (Wyckoff notation) in the AuBe$_5$ structure of the parent compound UCu$_5$. This leaves $L_2$ as originating from Cu$^{(4c)}$ nuclei; i.e., those sitting at the 4c site of the same structure. Unlike in UCu$_4$Pd, the appearance of signal from Cu$^{(4c)}$ nuclei in the Ni compound is clear evidence of site disorder in UCu$_4$Ni.

1. Introduction

UCu$_4$Ni is a non-Fermi liquid, quantum critical system, derived from dilution of Cu with Ni in antiferromagnetic (AFM) UCu$_5$ [1]. Introduction of Ni in the lattice structure of the parent compound suppresses the AFM transition temperature from 16.5 Kelvin down to zero at $x = 1$. This is very similar to the behavior of UCu$_{5-x}$Pd$_x$ upon dilution of Cu with Pd [2]. The Pd system has been the subject of extensive study (see e.g., references [2, 3, 4] and references therein). At first and for some time, the lattice structure of UCu$_4$Pd was considered to be ordered; Pd ions would occupy the 4c site of the AuBe$_5$ structure of UCu$_5$, and Cu would, in turn, occupy the 16e site (Wyckoff notation). However, the possibility of site disorder came after Cu-NMR measurements were performed in UCu$_{5-x}$Pd$_x$ ($x = 1, 1.5$) and interpreted as indicating the existence of inhomogeneity in the magnetic susceptibility [5]. Such inhomogeneity, which could also explain other thermodynamic and transport properties of the system [5, 6], can only come from Cu/Pd site interchange. Nevertheless, NMR only detected an unambiguous signal from one Cu site, which still leaves room for controversy regarding the amount of disorder (and its importance for the underlying physics) when derived from other measurements [7, 8]. Therefore, the existence of site disorder in UCu$_4$Pd could not be established directly, but only indirectly, by NMR alone.
The case of UCu$_4$Ni is somewhat different. The material was developed in part to understand the effects of disorder on the physics of quantum critical systems [1]. Because Ni ions are very similar in size to Cu ones (perhaps only slightly smaller), Ni can be expected to distribute itself randomly between the two available crystal sites creating strong site disorder. This expectation is consistent with resistivity and x-ray measurements, which display large values and broad spectra respectively [1]. Disorder in this material is also inferred in the work by López de La Torre et al [9], who have modeled the magnetic susceptibility of UCu$_4$Ni within the Kondo-Disorder [5] and Griffith Phase [6] pictures. Furthermore, it has been established by μSR measurements that the Ni system behaves similarly to UCu$_4$Pd down to the lowest temperatures [10]. Nevertheless, to date there has been no direct evidence for site disorder in UCu$_4$Ni.

In this paper, we present Cu-NMR spectra in a random powder of UCu$_4$Ni which clearly show the existence of Ni/Cu interchange between 4c and 16e sites. We find two unambiguous types of Cu-NMR lines with the necessary properties to demonstrate the phenomenon. By comparison with UCu$_4$Pd, we can directly identify one of the lines as coming from the nuclei sitting at site 16e, or Cu$^{(16e)}$. The “new” line in UCu$_4$Ni is therefore associated with nuclei at the 4c site, or Cu$^{(4c)}$. Furthermore, consistent with the point symmetry of these sites (trigonal for 16e and tetrahedral for 4c), we find that Cu$^{(16e)}$ nuclei are strongly affected by electric field gradients, whereas Cu$^{(4c)}$ nuclei experience little if any quadrupole effects. On the other hand, Cu$^{(4c)}$ nuclei seem to be strongly affected by the U magnetism. This makes the 4c site a particularly suitable Cu-NMR probe (not available in the Pd material) to study magnetic disorder effects in non-Fermi liquid, quantum critical, UCu$_5$−$_x$Ni$_x$.

2. NMR Spectra

2.1. Frequency Dependence at Low Temperature

![Figure 1](image1.png)  
**Figure 1.** Cu-NMR spectrum in UCu$_4$Ni at low frequency $\nu$ and low temperature $T$ as indicated. The spectral features labeled from A to H are described in the text.

![Figure 2](image2.png)  
**Figure 2.** Spectrum at higher value of $\nu$ but for the same value of $T$ as in Figure 1. Isotopic assignments are indicated to aid in identifying the lines described in the text.

Figure 1 presents the NMR spectra in UCu$_4$Ni at $T = 10$ K and $\nu = 43.7$ MHz (the lowest frequency at which spectra were obtained). As can be seen, there is substantial structure in the spectrum. The main and prominent (repeating) patterns correspond to signals from the two isotopes in naturally abundant Cu ($^{65}$Cu and $^{63}$Cu; expected abundance/intensity 30.9% and 69.1% respectively). The low intensity broad peaks on each side of the spectrum (labeled A and H) are made up mostly by signal from quadrupolar-satellite transitions of $^{63}$Cu. The corresponding satellites of $^{65}$Cu are not resolved. These satellites, together with features (B,D) and (E,G) constitute one type of NMR line which we refer to as $L_1$. The sets of features
(B,D) and (E,G) of $L_1$ are second-order quadrupole-split, central transitions of $^{65}\text{Cu}$ and $^{63}\text{Cu}$ respectively. $L_1$ has therefore two isotopic components, which we designate as $^{65}L_1$ and $^{63}L_1$ for $^{65}\text{Cu}$ and $^{63}\text{Cu}$ respectively. Features C and F constitute the second type of Cu-NMR line ($L_2$) found in this material—with corresponding isotopic components $^{65}L_2$ and $^{63}L_2$. The assignments become more clear after analyzing the frequency and temperature dependences of the spectral features, and matching them with the corresponding spectra in UCu$_4$Pd, as described below.

We compare the spectrum in Figure 1 with that displayed in Figure 2. The latter corresponds to the same low temperature of 10 K, but different frequency; i.e., $\nu = 67.71$ MHz (the highest frequency at which spectra were obtained). Using the notation introduced above, we observe first that the distance between A and H in field units remains approximately the same at higher frequencies. This yields a value of the quadrupolar frequency $\nu_Q = 12.6(5)$ MHz ($\nu_Q$ is proportional to the z-component of the electric field gradient tensor at the site where $^{63}L_1$ originates). In contrast, we can clearly see that lines from $^{65}\text{Cu}$ and $^{63}\text{Cu}$ are now separated by a larger amount. This follows directly from the fact that the main resonance frequencies are proportional to the applied field. More interestingly, the distance between B and D (of $^{65}L_1$), on the one hand, and E and G (of $^{67}L_1$), on the other, have decreased linearly with $1/\nu^2$, whereas the widths of C (of $^{65}L_2$) and F (of $^{63}L_2$) have increased in proportion to $\nu$. This behavior represents predominantly quadrupolar/electric-field-gradient effects for $L_1$ and spin/magnetic ones for $L_2$. There is no discernible sign that $L_2$ is affected by any quadrupole splitting.

2.2. NMR Spectra at Intermediate Frequency: Temperature Dependence

![Figure 3. Main Panel: Cu-NMR spectrum in UCu$_4$Ni at 53.60 MHz and $T = 10$ K as indicated. Inset: low-temperature spectrum in UCu$_4$Pd (from reference [11]) plotted on a similar scale as that of the main panel. A line of type $L_2$ is missing in UCu$_4$Pd.](image1)

![Figure 4. Main Panel: Cu-NMR spectrum in UCu$_4$Ni at 53.60 MHz and $T = 150$ K. Inset: high-temperature spectrum of UCu$_4$Pd plotted on a similar scale as that of the main panel. Again, a line of type $L_2$ is missing in UCu$_4$Pd.](image2)

The spectrum at $\nu = 53.60$ MHz and $T = 10$ K is presented in the main panel of Figure 3. At the same frequency, but for $T = 150$ K, the spectrum looks as depicted in the main panel of Figure 4. It is seen that the distances between B and D, and E and G, do not change appreciably as functions of temperature. This is consistent with the typical lack of $T$ dependence for quadrupole effects. On the other hand, the linewidths of C and F decrease noticeably as they should if affected by the sample paramagnetism. In effect, both types of lines ($L_1$ and $L_2$) experience line narrowing, in the sense that they become considerably sharper at higher temperatures. Since the quadrupole-split features remain at the same distance from each other, the narrowing of $L_1$ should therefore be magnetic in nature also.
3. Discussion

The behavior of the spectra with frequency and temperature variations is consistent with two types of Cu sites in UCu$_4$Ni. Nuclei at the site represented by $L_1$ are strongly affected by quadrupolar effects, whereas nuclei at the site represented by $L_2$ are not. In fact $L_1$’s behavior closely resembles that of the only line clearly resolved in UCu$_4$Pd (Insets in Figures 3 and 4), which represents the majority Cu site in that material; i.e., 16e. We therefore associate $L_1$ with Cu nuclei sitting at the 16e site of the crystal structure, or Cu$^{(16e)}$. Line $L_2$ is absent in the Pd material. Here, in the Ni case, this line could in principle be ascribed to some impurity phase, such as pure Cu or CuNi. In that case, however, one would expect very narrow and temperature independent line(s) near the field at which $2\pi\nu = \gamma H$ (where $\gamma/2\pi = 11.285$ MHz/T, and $H$ is the applied external field) [12]. However, it is seen that $L_2$ is strongly affected by frequency and temperature variations. The relaxation time of this signal is also seen to be shorter than that of pure Cu or CuNi phases whose intensity would be suppressed by the fast pulsing required in the current experiments (50 ms repetition times). This leaves $L_2$ as originating from Cu$^{(4c)}$ nuclei: those nuclei sitting at site 4c of the crystal structure. Unlike in UCu$_4$Pd, the appearance of a line from Cu$^{(4c)}$ nuclei in the Ni compound is clear evidence of site disorder in UCu$_4$Ni.

Our preliminary analysis of these data thus yields some quantitative measure of the different effects dominating the appearance of the spectra. In particular the value of $\nu_Q$ at Cu$^{(16e)}$, 12.6(5) MHz, should be compared with 10(1) MHz for the Pd compound [5]. This indicates stronger electric field gradients at the trigonal-symmetry 16e sites in the Ni sample. On the other hand, Cu$^{(4c)}$ nuclei are subjected to little if any electric field gradients, whereas they are strongly affected by the U paramagnetism. This would be consistent with the tetrahedral point symmetry of the 4c site, which would not allow and electric field gradient. The Cu$^{(4c)}$ nuclei are therefore very suitable to study magnetic disorder effects in UCu$_{5-x}$Ni$_x$ using NMR. That study will be reported elsewhere in the near future.

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