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NMR Investigation of antiferromagnetism and coherence in URu$_2$Si$_{2-x}$P$_x$

K. R. Shirer, M. Lawson, T. Kissikov, B. T. Bush, A. Gallagher, K.-W. Chen, R.E. Baumbach, and N. J. Curro

1Department of Physics, University of California, Davis, CA 95616, USA*
2National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310, USA

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We report $^{31}$P and $^{29}$Si NMR in single crystals of URu$_2$Si$_{2-x}$P$_x$ for $x = 0.09$ and $x = 0.33$. The spectra in the $x = 0.33$ sample are consistent with a homogenous commensurate antiferromagnetic phase below $T_N \sim 37$ K. The Knight shift exhibits an anomaly at the coherence temperature, $T^*$, that is slightly enhanced with P doping. Spin lattice relaxation rate data indicate that the density of states is suppressed for $x = 0.09$ below 30 K, similar to the undoped compound, but there is no evidence of long range order at this concentration. Our results suggest that Si substitution provides chemical pressure and electronic tuning mediated by filling of the s/p shells with minimal electronic inhomogeneity.

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The heavy fermion compound URu$_2$Si$_2$ has captured the attention of the condensed matter physics community for more than two decades. In recent years, several key experiments have shed new light on the nature of the hidden order phase in this material. However, one of the outstanding mysteries surrounding the nature of the hidden order is how it evolves into large-moment antiferromagnetic (AFM) order under pressure. Although there is a large anomaly in the specific heat and a partial gapping of the Fermi surface in the hidden order phase, there are no ordered moments. Hydrostatic pressure or Ru substitutions (chemical pressure) gives rise to large static moments with antiferromagnetic order. Chemical pressure offers an appealing alternative to studying the intrinsic physics of the hidden order and AFM phases can be uncovered through systematic doping studies.

An alternative approach is to tune the ground state by P, rather than Ru substitution. Recently Gallagher et al. have reported the synthesis of high quality single crystals of P doped URu$_2$Si$_2$ grown in indium flux. Hidden order in URu$_2$Si$_{2-x}$P$_x$ is completely suppressed by $x = 0.035$, followed by the emergence of a new phase by $x \sim 0.3$. Because P doping decreases the lattice size, it is natural to expect that P doping acts as chemical pressure and that the new phase is antiferromagnetic as is the case for the pure compound under pressure. It is also likely that P adds electrons, which may help to stabilize antiferromagnetism. Here we report detailed NMR studies that indicate that not only is this phase indeed AFM, but it is homogeneous and the ordered moment is comparable to that under pressure.

High purity single crystals of chemically substituted URu$_2$Si$_{2-x}$P$_x$ were grown using recently developed molten metal flux growth techniques described in Ref. 14. Single crystals of dimension \( \sim 500 \mu \text{m} \) and mass \( \sim 0.1 \) mg were selected for detailed studies with concentrations of $x = 0.09$ and $x = 0.33$. Magnetic susceptibility was measured in an applied field of $H = 5 \text{ kOe}$ parallel the $c$-axis of mosaics of single crystals for temperatures $T = 1.8$-350 K. $^{31}$P nuclear magnetic resonance (NMR) spectra ($I = 1/2$, natural abundance 100\%) were acquired by measuring spin echoes as function of field applied parallel to the $c$-axis of single crystals at a fixed frequency of 118.315 MHz. The spin-lattice relaxation rate, $T_1^{-1}$, was measured at the center of the spectra as a function of temperature. We estimate approximately $1 \times 10^{16}$ and $4 \times 10^{16}$ $^{31}$P nuclei for each sample, which exceed the number of naturally-abundant $^{29}$Si nuclei. These numbers are close to the limit of detection for NMR, thus several thousand echoes were signal averaged over several days in order to achieve sufficient signal to noise ratios.

![Figure 1](image_url)
Fig. 1 presents a series of P NMR spectra at various temperatures at fixed frequency. In the paramagnetic phase, there is a single P resonance at frequency \( f = \gamma H_0(1 + K_x) \), where \( \gamma = 17.236 \text{ MHz/T} \) is the gyromagnetic ratio and \( K_x \) is the Knight shift. The inhomogeneous FWHM is \( \sim 80 \text{ Oe} \), and the \( \pi/2 \) pulse width for the echoes was 1.6\( \mu \text{s} \). The \( x = 0.09 \) doping shows a smooth evolution of the spectra with no splitting of the peak down to 4K, indicating the absence of any static internal magnetic fields.\(^{13}\) For \( x = 0.33 \) the spectrum evolves smoothly down to \( \sim 50 \text{ K} \), below which the spectral weight is reduced, most likely due to an enhanced spin echo decay rate, \( T_2^{-1} \). This enhancement reflects the slowing down of spin fluctuations at the onset of long-range antiferromagnetic order below \( T_N \sim 37 \text{ K} \), in agreement with specific heat measurements.\(^{14,16}\)

The spectra at 5K and 20K at this doping reveal two separate peaks, indicating the presence of a static internal field, \( H_{\text{int}} \), that is either parallel or perpendicular to the applied field. There is no evidence of a third central peak, in contrast to \(^{29}\)Si NMR measurements in the large moment AFM phase of \( \text{URu}_2\text{Si}_2 \) under pressure and in \( \text{URu}_{2-x}\text{Rh}_x\text{Si}_2 \).\(^{12,13}\) The latter two systems are inhomogeneous with antiferromagnetic patches coexisting with paramagnetic/hidden order regions.\(^{17}\) The absence of the central line in \( \text{URu}_2\text{Si}_{2-x}\text{P}_x \) indicates a homogeneous antiferromagnetic state in the vicinity of the P dopants. It is possible that the AFM order is reduced or absent for regions far from the P dopants; however at this doping level the nearest neighbor P-P distance is just over a lattice constant. Since any variation of the AFM must occur at a length scale of the coherence length, which is much longer than a unit cell in the ordered phase, the data strongly suggests that the AFM order is essentially uniform over the entire volume.

In order to investigate the nature of the distribution of internal fields, we simulate the NMR spectrum for an incommensurate spin density wave. If the internal field is incommensurate and varies spatially with wavelength \( \lambda \) and amplitude \( H_{\text{io}} \), then the theoretical lineshape is given by \( P(\omega) = \left( \frac{\lambda \gamma H_{\text{io}} \sqrt{1 - ((\omega - \gamma H_0)/\gamma H_{\text{io}})^2}}{1} \right)^{-1} \), where \( \gamma \) is the gyromagnetic ratio and \( H_0 \) is the external applied field.\(^{18,19}\) The dotted line shown in Fig. 1 is computed by convoluting a Gaussian with \( P(\omega) \). It is clear that the incommensurate model does not fit the data. In fact, the spectral intensity vanishes between the two split peaks,\(^{20}\) and the spectrum is better fit to two Gaussians at frequencies \( \gamma(H_0 \pm H_{\text{int}}) \). This result implies that the incommensurate magnetic order, neutron scattering reveals ordered U moments oriented along the c-direction with wavevector \( \mathbf{Q}_{\text{AF}} = (1, 0, 0) \).\(^{21}\)

The internal field, \( H_{\text{int}} = \Delta f/2\gamma \) where \( \Delta f \) is the peak splitting, is shown in Fig. 2. Similar values were reported at the Si site in \( \text{URu}_2\text{Si}_2 \) under pressure,\(^{14}\) and in the Rh-doped material.\(^{15}\) If we assume a simple relationship between the ordered moment and the internal field: \( H_{\text{int}} = B S_0 \), where \( B \) is the hyperfine coupling and \( S_0 \) is the ordered U moment, we use a hyperfine coupling of 4 kOe/\( \mu_B \).\(^{22}\) We estimate an ordered moment of \( 0.22 \pm 0.01 \mu_B/\text{U} \). This value, however, is less than that reported by neutron scattering which find \( S_0 \sim 0.4 \mu_B/\text{U} \).\(^{21}\) We estimate the direct dipolar field from the ordered U is \( \sim 0.5 \text{ kG along } (001) \). The discrepancy is likely related to a more complex hyperfine coupling between the Si/P nuclei and the five nearest neighbor U moments.

The spectra in Fig. 1 show a clear evolution of the Knight shift, which is shown in Fig. 3. The Knight shift in the pure compound (acquired in an aligned powder) has been scaled to match our previous results in single crystals.\(^{23,24}\) For the \( x = 0.09 \) sample, both Si and P were measured at 25K, and the data coincide, as seen in Fig. 3. This fact is important because it indicates...
that both the Si and the P are probing the same physics, and it is appropriate to compare data measured at the two crystallographically identical sites. All three samples exhibit similar trends, with maxima around 50 K. For the \( x = 0.33 \) sample the shift in the antiferromagnetic state was determined by the average of the split resonances, assuming that \( H_{int} = 0 \).

Figure 4 shows the Knight shift versus susceptibility with temperature as an implicit parameter. In URu$_2$Si$_2$, as in most heavy fermion systems, the Knight shift arises because the nuclear spins \( I \) couple both to the itinerant electron spins, \( S_c \), and to the localized \( f \) moments, \( S_f \): \( H_{HF} = A I \cdot S_c + B I \cdot S_f \), where \( A \) and \( B \) are the hyperfine couplings.\textsuperscript{23} The Knight shift is given by: \( \chi = \chi_{cc} + 2 \chi_{cf} + \chi_{ff} \). At high temperatures, both \( K \) and \( \chi \) are proportional to one another, as seen in Fig. 4. The solid lines are linear fits to the high temperature data, and the fit parameters are summarized in Table I. The slope of the high temperature linear fit yields the transferred hyperfine coupling, \( B \), and the intercept \( K_0 \) is a temperature independent offset that is usually given by the orbital susceptibility and diamagnetic contributions.\textsuperscript{25} It is noteworthy that the hyperfine coupling to the P is nearly identical to the coupling to the Si, which suggests that the local electronic structure is not significantly perturbed by the presence of the dopant. The variation in the \( K_0 \) parameter may also be related to errors in measurement of the susceptibility due to the very low masses of the crystals.

Below the coherence temperature, \( T^* \), the linear relationship between \( K \) and \( \chi \) breaks down as \( \chi_{cf} \) grows in magnitude.\textsuperscript{23,26} This quantity reflects the heavy electron component in the two-fluid model that emerges due to collective hybridization.\textsuperscript{27-31} To examine the temperature dependence of the heavy electron susceptibility, we compute \( K_{HF} = K - K_0 - B \chi = (A - B)(\chi_{cf} + \chi_{cc}) \), as shown in Fig. 5. It has been shown that \( K_{HF} \) scales universally with \( T/T^* \), where \( T^* \) is material dependent, and that \( T^* \) agrees well with several other experimental measurements of the coherence temperature of the Kondo lattice.\textsuperscript{32} The solid lines in Fig. 5 are fits to the empirical two-fluid expression:

\[
K_{HF}(T) = K_0^0(1 - T/T^*)^{3/2}[1 + \log(T^*/T)] \tag{1}
\]

where \( K_0^0 \) is a constant. \( T^* \) is given in Table I. We find that \( T^* \) agrees well with resistivity measurements, which reveal only a modest \( \sim 5\% \) increase in \( T^* \) over this doping range.\textsuperscript{15} Surprisingly, however, \( K_{HF} \) decreases below 20 K for the \( x = 0.09 \) sample. This ‘relocalization’ phenomenon has been observed previously in other heavy fermion antiferromagnets, and may reflect a precursor to the emergence of local moment order at higher dopings.\textsuperscript{23,33} In this case, however, relocalization is not evident in the AFM \( x = 0.33 \) sample.

We have also measured the spin-lattice-relaxation rate as a function of temperature at the \( P \) site, as shown in Fig. 6, which includes data for the Si in pure URu$_2$Si$_2$. Both $^{29}$Si and $^{31}$P are spin 1/2 nuclei, and the magnetization recovery data were well fit by the standard recovery function, \( M(t) = M_0(1 - f e^{-t/T_1}) \), where \( M_0 \) is the equilibrium magnetization and \( f \) is the inversion

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**TABLE I. Doping, hyperfine parameters, and coherence temperatures in URu$_2$Si$_{2-x}$P$_x$.**

| \( x \) | nucleus | \( B \) (kG/\( \mu_B \)) | \( K_0 \) (%) | \( T^* \) (K) |
|---|---|---|---|---|
| 0  | $^{29}$Si | 4.34±0.10 | -0.08 ± 0.02 | 73.1±0.5 |
| 0.09 | $^{31}$P | 3.05±0.07 | -0.10 ± 0.14 | 74.2±1.6 |
| 0.33 | $^{31}$P | 3.89±0.08 | -0.09 ± 0.01 | 73.2±0.3 |

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**FIG. 4.** (color online) Knight shift versus the magnetic susceptibility in URu$_2$Si$_{2-x}$P$_x$ with \( x = 0, 0.09, \) and 0.33. Solid lines are fits to the high temperature data as described in the text.

**FIG. 5.** (color online) \( K_{HF} \) versus temperature in URu$_2$Si$_{2-x}$P$_x$. The solid lines are fits to Eq. 1, and the dashed vertical lines indicate \( T_{HO} \) for \( x = 0 \), and \( T_N \) for \( x = 0.33 \).
It is noted that the relocalization below 20K is nearly twice as large as the Si in the pure URu2Si2, even after scaling by the square of the gyromagnetic ratios. This difference could be related to form factors and hyperfine coupling differences to the P and the Si. It is also possible that the spin fluctuations are higher in the P doped samples, however the temperature dependence of $(T_1T)^{-1}$ above 50K is nearly identical for all three systems, which suggests otherwise. Furthermore, $(T_1T)^{-1}$ has been observed to decrease under pressure in the pure URu2Si2. A third possibility is that the local density of states is slightly different at the P site.

In summary, we have performed $^{31}$P NMR measurements in single crystals of URu2Si2-$x$P$_x$ with $x = 0.09$ and 0.33. For the AFM $x = 0.33$ crystal, we determined $T_N = 36.6 \pm 1.8$ K with a commensurate internal field $H_{int} \sim 0.85$ kOe oriented along the c direction at 5 K. This behavior is entirely consistent with the large moment AFM phase in pure URu2Si2 under pressure. Furthermore, we find that the AFM phase in URu2Si2-$x$P$_x$ is homogeneous, in contrast to the heterogeneous patches of AFM observed in the URu2Si2 under pressure and U(Ru,Rh)$_2$Si$_2$, and possible phase segregation observed in URu2(Si,Ge)$_2$. We find the $x = 0.09$ crystal undergoes no phase transition, but the $(T_1T)^{-1}$ data for this crystal reveal a partial suppression of the density of states. All three compounds exhibit a Knight shift anomaly at $T_* \sim 72$K. For the $x = 0.09$ crystal, the heavy electron component of the Knight shift is reduced below 20 K, suggesting a relocalization of the moments as the system is tuned toward long range antiferromagnetic order for sufficiently large P doping. Our results indicate that P doping offers an avenue to tune the ground state properties cleanly, without inducing an inhomogeneous electronic response.

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