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# $^{31}$P NMR investigations on the ferromagnetic quantum critical system YbNi$_4$P$_2$

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We studied the heavy-fermion system YbNi$_4$P$_2$, which presents strong ferromagnetic correlations, using the local $^{31}$P NMR probe over a wide field (0.2–8.6 T) and temperature (1.8–200 K) range. The $^{31}$P NMR Knight shift provides the static spin susceptibility which tracks the bulk susceptibility whereas the spin-lattice relaxation rate $^{31}(1/T_1)$ provides information about the fluctuations of the Yb $4f$ moment. The Korringa law is valid over a wide range of temperature and field. The Korringa product $^{31}(1/T_1TK^2S_0) \ll 1$ gives evidence for the presence of strong ferromagnetic correlations. A $^{31}(1/T_1T) \sim T^{-3/4}$ behavior was found over two decades in temperature.

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Recently quantum criticality (QC) has emerged as a central topic, especially in solid state physics. While in the $4f$- and $5f$-based systems close to an antiferromagnetic (AFM) ordering QC is well established from experimental and theoretical points of view, the observation of ferromagnetic quantum criticality (FMQC) remains scarce and is mostly limited to $3d$ and $5f$ electron systems.[1–5] Ferromagnetic quantum criticality (FMQC) has been discussed among some $3d$-based weak itinerant ferromagnets such as ZrZn$_2$ (Ref. 5) and NbFe$_2$,[6] and $5f$-based systems such as UGe$_2$ (Ref. 7) or UCoGe.[8] In contrast, among $4f$ systems it is rarely discussed.[9–11]

In proximity to a quantum critical point (QCP), unconventional power-law behavior in resistivity [$\rho(T) \sim T^n (n < 2)$], magnetic susceptibility [$\chi \sim -\ln T$ or $T^{-n} (n < 1)$], and specific heat [$C/T \sim -\ln T$ or $T^{-n} (n < 1)$] could be observed experimentally, which is indicative of deviations from standard Fermi-liquid (FL) theory[12] and leads to the concept of the non-Fermi-liquid (NFL) state. NFL behavior is fully developed in the proximity of the QCP, but even far away from the QCP the microscopic and macroscopic properties are influenced in some temperature window. Therefore the normal-state properties must also be scrutinized in order to understand the diverse properties of QC, especially with some microscopic tool. Furthermore, the lack of systematic NMR investigations on FMQC systems in general to comprehend the spin dynamics also lead us to investigate these types of systems in great detail.

The standard theory of Moriya for itinerant magnets predicts for a three-dimensional (3D) FM criticality close to the QCP for the spin susceptibility (and spin-lattice relaxation rate) $\chi_Q \sim 1/T_1T \sim T^{-n}$ $(n = 4/3)$.[13–15] Nonetheless such "clean" behavior is very rare (see, for example, UCoGe).[8] For more localized $4f$-based Ce or Yb systems FMQC has been little discussed. Furthermore, here, the formation of a so-called "quantum Griffiths" phase or a Kondo cluster state originating from small disorder is discussed.[16] The ferromagnet CePd$_{1-x}$Rh$_x$ seems to be the prototype of this sort of magnetism.[17] Here scaling in $C$, $\chi$, $M$, and $1/T_1$ could be found, which eventually should lead to $n < 0.5$ in $1/T_1T$. Another possibility is the fragile interplay of both FM and AFM correlations in these systems. One example of that is YbRh$_2$Si$_2$, where AF order at $T_N = 70$ mK was found. Nonetheless, NMR and electron spin resonance (ESR) studies reveal the presence of additional FM correlations which are promoted by magnetic fields. Here the system develops strong ferromagnetic correlations evidenced by the NMR investigations with a $^{29}(1/T_1T) \sim T^{-0.5}$ power law associated with the NFL behavior.[18] Despite the presence of both FM and AFM correlations the system behaves very locally and the Korringa law is valid.

YbNi$_4$P$_2$ is a recently discovered heavy-fermion Kondo lattice with an extremely reduced Curie temperature ($T_C = 0.17$ K) due to strong Kondo screening, $T_K \sim 8$ K, in close proximity to a FM QCP.[19] The crystal structure is quasi-one-dimensional with Yb$^{3+}$ chains along the $c$ axis of the tetragonal unit cell. Between 50 and 300 K, the magnetic susceptibility follows a Curie-Weiss law with stable Yb$^{3+}$ moments. A pronounced drop in resistivity below 30 K indicates the onset of coherent Kondo scattering, confirmed in a pronounced minimum of the thermopower. Detailed low-temperature ac susceptibility measurements reveal a sharp FM transition at $T_C$, confirmed in the specific-heat data which presents a distinct $\lambda$-type anomaly at $T_C$. Below $T_C$, a heavy FL ground state is reflected in a constant Sommerfeld coefficient, $\gamma_0 = 2$ J/mol K$^2$.[19] Therefore this is a promising candidate for a prototype Yb-based FM system close to quantum criticality.

In this Rapid Communication we report $^{31}$P NMR measurements on the stoichiometric compound YbNi$_4$P$_2$. The Knight shift $^{31}K$ and the nuclear spin-lattice relaxation rate $^{31}(1/T_1)$ were measured over a wide field range of 0.2–8.6 T to inspect the strong FM correlations suggested by the bulk measurements. Being a local probe, NMR can shed light on microscopic magnetic properties by analyzing $^{31}K$ and $^{31}(1/T_1)$. $^{31}K$ gives information about the uniform static spin susceptibility $\chi'(\mathbf{q} = 0)$, while $^{31}(1/T_1T)$ reveals the spin-fluctuation character from the $\mathbf{q}$-averaged dynamical spin susceptibility $\chi''(\mathbf{q},\omega)$. In the conventional FL state, both $^{31}K$ and $^{31}(1/T_1T)$ are $T$ independent, and the Korringa relation, $1/T_1TK^2 = S =$ const, is valid. In the concept of renormalized heavy quasiparticles, the ground state for $T \rightarrow 0$, far below the Kondo temperature ($T_K$), is the FL state where $K$ and $1/T_1T$ are constant ("Kondo saturation") and the Korringa law is also valid. Far above $T_K$, $^{31}K$ and $^{31}(1/T_1T)$ become $T$ dependent, but if the coupling mechanism between NMR nuclei and the local magnetic moment of the $4f$ ion is the same for static and dynamic NMR responses, the Korringa law could still be valid. Deviations from the $T$-independent behavior of $^{31}K$ and $^{31}(1/T_1T)$ at lower temperature usually

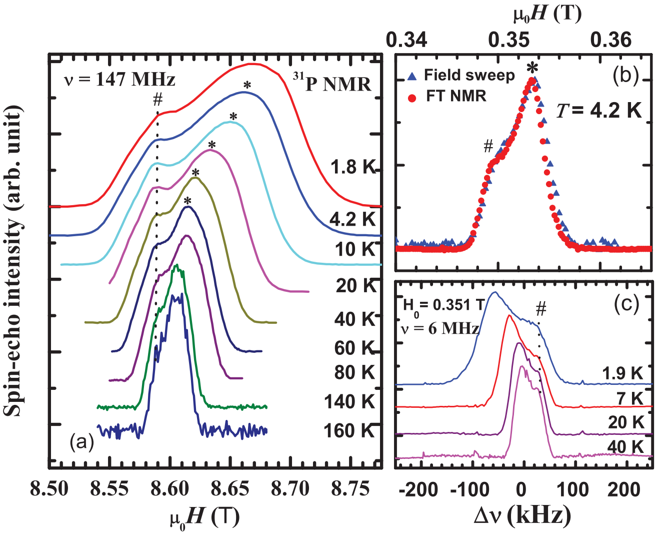

FIG. 1. (Color online) (a) $^{31}$P field-sweep NMR spectra at 147 MHz at different temperatures (* marks the maximum position used for the shift calculation whereas # marks the nonmagnetic impurity $Ni_3P$). (b) Comparison of the $^{31}$P field-sweep NMR and FT-NMR spectra taken at 4.2 K and 6 MHz. (c) $^{31}$P FT-NMR spectra at different temperatures at 6 MHz corresponding to the field 0.351 T.

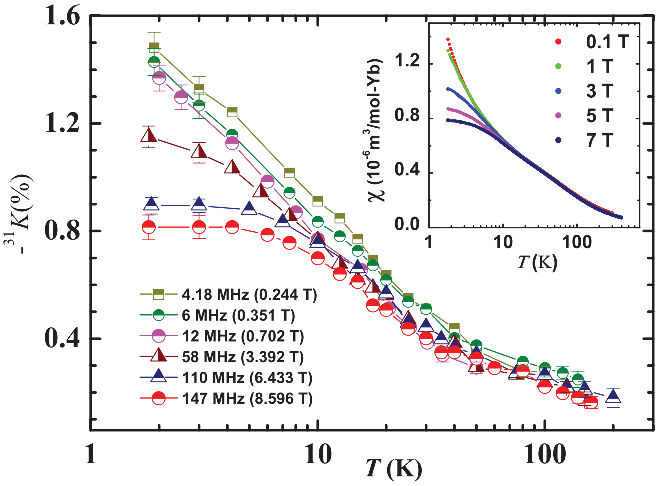

FIG. 2. (Color online) $^{31}K(\%)$ as a function of temperature for $YbNi_4P_2$ at different frequencies (fields), as indicated. The field values are calculated from a NMR resonance frequency using $^{31}\gamma/2\pi = 17.10$ MHz/T. The inset shows the temperature vs susceptibility plot at different fields, as indicated. The fields are chosen similar to the NMR fields.

point toward the vicinity of a quantum critical point and are interpreted as NFL behavior, in analogy to the unconventional power laws observed in bulk properties in the NFL systems.

Figure 1(a) shows the $^{31}$P NMR powder spectra taken at 147 MHz. The powder spectra is a superposition of two lines. One line (marked by #) shows no shift with temperature and it is associated with a small amount of nonmagnetic impurity phase ($<5\%$) $Ni_3P$. The $Ni_3P$ phase is nonmagnetic and has a much longer relaxation time than the P in the $YbNi_4P_2$ phase.[20] Therefore the weight in the powder spectra depends on the NMR time scale of the experiments. At low fields where $T_1$ of $YbNi_4P_2$ gets longer we analyzed the spectral weight and confirmed the $<5\%$ impurity contribution. The main line comes from $^{31}$P in $YbNi_4P_2$ and shows a magnetic negative shift and a line broadening toward lower temperatures. A negative shift is expected from the simple conduction electron polarization model for Yb $4f$ ions.[21] Due to the fact that sizable single crystals for NMR are not available, the shift has been determined from powder results by using the center position of the higher intensity peak (*) with respect to the reference line marked by (#). Making use of the presence of nonmagnetic $Ni_3P$ with $^{31}K = 0$ gives very accurate shift values, especially for small fields where remanent fields of the magnet usually create great problems in an exact shift determination. Furthermore, we used $H_3PO_3$ with $^{31}K = 0$ as a reference compound for the absolute shift determination at high fields. The aim of this Rapid Communication is to probe the critical fluctuation and/or the Kondo fluctuation in the zero-field limit. Therefore field-sweep (FS) NMR measurements are performed at very low fields. Here the linewidth is strongly reduced and the FS method is at its limits. To overcome this problem we switched to the more sensitive Fourier transform (FT) NMR method. In Fig. 1(b) the comparison of the $^{31}$P NMR spectra taken at FS (6 MHz) and the FT method (0.351 T) is plotted after normalization to the field axis. This plot confirms that these two different methods ultimately give the same results. For the low frequencies 4 and 6 MHz we used therefore only the FT-NMR method. As an example FT spectra at 6 MHz at a center field $H_0 = 0.351$ T are shown in Fig. 1(c).

Figure 2 displays the $^{31}K(T)$ vs $T$ plot. $^{31}K(T)$ shows good agreement with the bulk magnetic susceptibility. At low fields (0.244, 0.351, and 0.702 T), $^{31}K$ increases monotonously when lowering the temperature down to 1.8 K without any sign of saturation. However, at higher fields (6.433 and 8.596 T), $^{31}K(T)$ starts to saturate toward lower temperature. Additionally the onset of the saturation is shifted toward higher temperatures with increasing fields. Figure 2 (inset) shows the susceptibility versus $T$ plot at different fields, as indicated. This plot is consistent with the $^{31}K(T)$ vs $T$ plot. Therefore this rules out the presence of any magnetic (FM and/or AFM) impurity contribution in $\chi(T)$. The hyperfine coupling constant ($A_{\mathrm{hf}}$) is estimated by plotting $^{31}K(T)$ with respect to bulk susceptibility (not displayed here). The value of $A_{\mathrm{hf}}$ is 592 Oe/$\mu_B$, which is close to the value obtained for $YbRh_2Si_2$.[18] The saturation of $^{31}K$ below 8 K for 6.433 and 8.596 T can be interpreted as the polarization effect of the external field on the $Yb^{3+}$ localized moment. At around 80 K a shoulder is observed in the $^{31}K(T)$ vs $T$ plot, which is likely caused by crystal electric field (CEF) excitations. A similar feature is also observed in the susceptibility data.

Now we present nuclear spin-lattice relaxation rate $^{31}(1/T_1)$ data on $YbNi_4P_2$. $^{31}(1/T_1)$ measurements were performed as a function of temperature at different frequencies 12, 58, and 147 MHz (corresponding to the fields 0.702, 3.392, and 8.596 T, respectively) by exciting at the maximum of the anisotropic NMR spectra (marked by ⋆ in Fig. 1). The nuclear magnetization recovery curves could be fitted at any temperature and field with a standard single exponential function expected for $I = 1/2$ NMR nuclei. This indicates that the system has a single relaxation channel for a particular field.

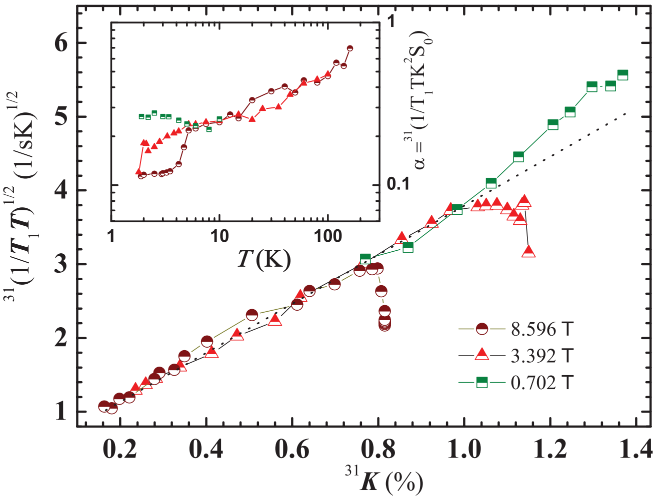

FIG. 3. (Color online) $^{31}(1/\sqrt{T_1T})$ as a function of $^{31}K(\%)$ at different fields, as indicated. The dotted line indicates the linear $^{31}K(T)$ dependence. At high $^{31}$K values (low temperatures) the experimental data show an upward turn for low fields due to critical fluctuations, and a downward turn for high fields due to a field polarized state. The inset shows the $T$ dependence of the Korringa product $\alpha = {}^{31}(1/T_1TK^2S_0)$ (see text).

Before starting the rather complex discussion of the $H$ and $T$ dependence of $^{31}(1/T_1)$ we first raise the question whether this system is an itinerant or a more localized system. For a localized system the Korringa theory should be applicable, whereas for an itinerant system results should be discussed in the framework of the Moriya theory. Evidence for YbNi$_4$P$_2$ being a local system comes from the susceptibility data of Krellner *et al.*, giving proof for a full Yb$^{3+}$ moment above 150 K.[19] The ultimate NMR probe is the $^{31}K$ dependence of $^{31}(1/T_1T)$. If $^{31}(1/T_1T) \sim {}^{31}K^2$ is observed, then the Korringa law is valid, whereas a linear $^{31}K$ dependence points toward an itinerant system where the Moriya theory should be applied.[22]

Figure 3 shows the $^{31}[1/\sqrt{(T_1T)}]$ vs $^{31}K$ plot for three different fields. For high fields (8.596 and 3.392 T) they follow almost linear behavior, except at low temperature, where due to the field polarized state, a bending occurs (see below). The dotted line in Fig. 3 is the guide to the linear dependency. The almost linear relation between $^{31}[1/\sqrt{(T_1T)}]$ and $^{31}K$ indicates the validity of the Korringa law, which means that one has to consider the localized moment framework. Even though this was already evidenced by the bulk measurements, now it is also clear from the viewpoint of a local picture. However, at low fields (0.702 T) a clear upward deviation from the linearity is observed, which is likely related to the development of critical magnetic fluctuations originating from the fragile interplay of Kondo and FM correlations. It should be mentioned that the above described behavior is reminiscent of YbRh$_2$Si$_2$. There a similar behavior is observed but with the difference that AFM order shows up at low $T$ ($T_N = 70$ mK). Therefore we have plotted in Fig. 4 the temperature dependence of $^{31}(1/T_1T)$ and the $^{31}(1/T_1)$ on a double log scale in the main panel and inset, respectively, together with $^{29}$Si NMR data of YbRh$_2$Si$_2$ (at 2.42 T) taken from Ref. 18. Interestingly the results look very similar to those of YbNi$_4$P$_2$ at around 3.392 T.

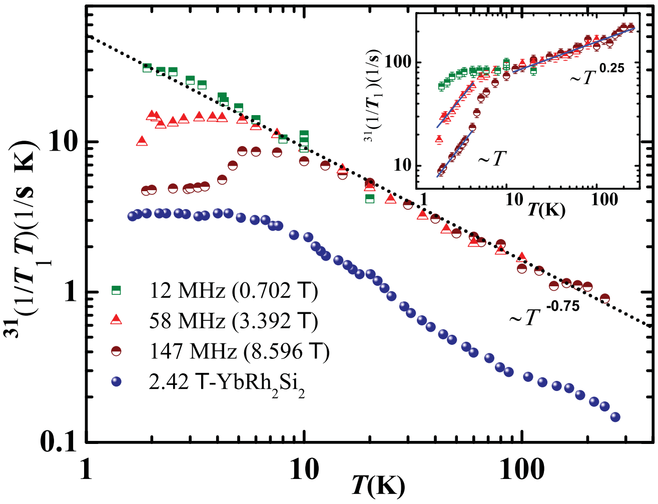

FIG. 4. (Color online) $^{31}(1/TT_1)$ vs $T$ plot at different fields, as indicated. The blue circles represent the $^{29}$Si NMR data for YbRh$_2$Si$_2$ at 2.42 T (Ref. 18) after multiplying by $(A_{\mathrm{hf}}^2\gamma^2)_{\mathrm{P}}/(A_{\mathrm{hf}}^2\gamma^2)_{\mathrm{Si}}$. The inset shows the $^{31}(1/T_1)$ as a function of temperature at different fields, as indicated.

A considerable field (frequency) dependence of $^{31}(1/T_1T)$ is observed below 10 K, in agreement with the $^{31}K$, $\chi(T)$, and $C(T)$ results. Above 10 K, $^{31}(1/T_1T)$ follows a $T^n$ power law with $n$ smaller than $-1$ ($n = -\frac{3}{4}$) over two decades in temperature. By further lowering the temperature, $^{31}(1/T_1T)$ deviates from this ($n = -\frac{3}{4}$) power law and becomes constant, leaving a broad maximum. Though the occurrence of such a weak power law over a wide temperature and field range is rare, nonetheless it is found for systems such as USb$_2$, CeCoIn$_5$, YbAuCu$_4$, and therefore could not be simply justified as an accident.[23–25] For a local moment $4f$ system far from the critical point such behavior is unusual. For example, in a $4f$ heavy fermion, such as CeCu$_2$Si$_2$, $(1/T_1T)$ levels at a constant value ("Kondo saturation") just below the Kondo temperature $T_K$ and above $T_K$ in most cases, a $n = -1$ power law (constant $1/T_1$ behavior) is observed.[26,27] In contrast to that, in the two Yb-based correlated systems, YbRh$_2$Si$_2$ and YbNi$_4$P$_2$, there is no Kondo saturation and a $n < 1$ power law is observed. The absence of the "Kondo saturation" might be related to the presence of ferromagnetic correlations whereas the high-temperature behavior might originate from the CEF splitting. The validity of the Korringa law suggest that the non-Curie-Weiss behavior of the static susceptibility toward lower temperatures caused by CEF splitting is responsible for the $1/T_1T$ behavior.

For free-electron metals the Korringa relation is given by $1/T_1TK^2 = S_0 = \pi\hbar\gamma_N^2k_B/\mu_B^2$, where $\gamma_N$ is the nuclear gyromagnetic ratio of $^{31}$P and $k_B$ is the Boltzmann constant. Including electronic correlations leads to the modified Korringa relation $1/T_1TK^2 = S = \alpha S_0$. The so-called Korringa product $(1/T_1TK^2S_0) = \alpha$ is a very useful probe for correlations, where $\alpha = 1$ indicates the absence of correlation, whereas $\alpha > 1$ indicates an AFM correlation and $\alpha < 1$ FM correlation. For the $^{31}$P nuclei $S_0$ is $0.623 \times 10^6$ 1/sK while experimentally we found $0.133 \times 10^6$ 1/sK at 2 K. This gives a value of $\alpha(2\ \mathrm{K}) \simeq 0.21$, which indicates ferromagnetic correlations such as in $YbRh_2Si_2$ ($\alpha = 0.11$ at 100 mK) or such as in CeFePO($\alpha = 0.065$).[18,28] This is also consistent with the strongly enhanced Sommerfeld-Wilson ratio $W_{T\rightarrow 0.3\ \mathrm{K}} \cong 20$ found for $YbNi_4P_2$.[19] The inset of Fig. 3 shows the temperature and field dependency of $\alpha$.

In summary, we have presented a $^{31}$P NMR study on the recently discovered heavy-fermion Kondo lattice system $YbNi_4P_2$ to shed some light on its microscopic properties. At low fields $^{31}K(T)$ and $^{31}(1/T_1T)$ show no signs of saturation toward low temperatures, in contrast to a heavy FL state well below $T_K = 8$ K. On the contrary, the Korringa law is valid over a wide field and temperature range. Below 10 K and at low fields the breakdown of the Korringa law points toward the onset of a critical ferromagnetic fluctuation. In contrast to Ce heavy-fermion systems, but very similar to $YbRh_2Si_2$, $^{31}(1/T_1T)$ shows a weak power law with $1/T_1T \sim T^{-n}$, with $n < 1$ down to the lowest temperatures. We speculate that the $^{31}(1/T_1T)$ behavior could be associated with the CEF splitting changing the effective magnetic moment of the system. Moreover, the value of the Korringa product being smaller than one strongly suggests the presence of FM correlations. At low fields, $^{31}(1/T_1T)$ results indicate the development of critical fluctuations. $YbNi_4P_2$ is still not completely understood. NMR measurements should be extended toward lower temperature and single crystals are required to investigate the magnetic anisotropy. Furthermore, inelastic neutron-scattering studies are required to investigate the **q** dependence of the fluctuations. Interestingly, for $YbRh_2Si_2$, inelastic neutron studies strongly reveal the presence of two relaxation channels. Experimentally at low temperatures the quasielastic linewidth has been found to have two components, one constant component (Kondo fluctuation) and one depending linear on $T$ (intersite fluctuations).[29] It would be rather interesting to see if neutron studies on $YbNi_4P_2$ show similar features.

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