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^{31}P-NMR study of the uranium-based filled skutterudite compound UFe$_4$P$_{12}$

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^{31}P NMR measurements have been performed on the uranium-based ferromagnetic insulator UFe$_4$P$_{12}$ with $T_C=3.15$ K. The field-orientation dependence of the hyperfine interaction has been measured using a single crystal, and the results compared with a point-dipolar field calculation assuming local moments at the U sites. We have also measured the field and temperature dependence of the nuclear spin-lattice relaxation rate $(1/T_1)$ in several fields between 1.0 and 5.5 T at temperatures between 1.4 and 300 K. The results are discussed on the basis of a localized picture for the uranium $5f$ electrons.

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I. INTRODUCTION

Recently Pr-based filled skutterudite compounds with a $4f^2$ electron configuration, such as PrOs$_4$Sb$_{12}$ (Ref. 1) and PrFe$_4$P$_{12}$, have attracted a great deal of attention.[2] The ground state of Pr^{3+} ($4f^2$, $J=4$) in a cubic crystalline electric field (CEF) is believed to be a nonmagnetic Γ_1 singlet.[3,4] The heavy fermionlike behavior found in these compounds is considered to be suggestive of a quadrupolar Kondo lattice, in analogy with the quadrupolar Kondo model.[5] On the other hand, the $5f^2$ electron configuration is also expected to be realized in the tetravalent U^{4+} state. In the family of filled skutterudites, however, the only U-based compound successfully crystallized to date is UFe$_4$P$_{12}$.[6,7] There is no other filled skutterudite including $5f$ electrons reported up to now.

UFe$_4$P$_{12}$ is isostructural with PrFe$_4$P$_{12}$, except for the replacement of Pr by U. The lattice constant is 7.7729 Å, which is the smallest value of all the filled skutterudite compounds. Magnetization measurements suggested the occurrence of ferromagnetic ordering with a relatively low Curie temperature $T_C \sim 3$ K.[6,7] This ferromagnetic ground state was later verified by neutron diffraction measurements.[8] On the other hand, the electrical resistivity increases nearly 7 orders of magnitude as T is lowered from room temperature to liquid helium temperatures.[6,7] These results reveal that UFe$_4$P$_{12}$ is a ferromagnetic insulator, and it has been suggested that this insulating behavior may arise from strong f-electron hybridization.[6]

More recently, Matsuda, *et al.*, have performed detailed specific heat, magnetic susceptibility, and also high-field magnetization measurements using a single crystal.[9] Their experimental results were found to be consistent with the crystalline electric field scheme for T_h site symmetry, assuming a $5f^2$ configuration for the U. The possible CEF scheme is suggested to be (i) a Γ_1 ground state and a Γ_4 first excited state, separated by 6 K, or (ii) a Γ_4 ground state and a Γ_{23} first excited state, separated by 800 K. In both cases, the whole scale of the CEF splitting of $5f^2$ is found to be much larger than that of the Pr state in the Pr-based filled skutterudite compounds.

In this paper, we report microscopic magnetic properties of UFe$_4$P$_{12}$ obtained via ^{31}P NMR measurements. The results of NMR shift and spin-lattice relaxation rate $(1/T_1)$ measurements are discussed on the basis of a localized picture for the uranium $5f$ electrons. This is a NMR study of a filled skutterudite compound containing $5f$ electrons.

II. EXPERIMENTAL

Single crystals of UFe$_4$P$_{12}$ were grown by a Sn-flux method described in detail elsewhere.[9] The ^{31}P NMR measurements were carried out using a superconducting magnet and a phase coherent, pulsed spectrometer. The temperature dependence of the NMR shift was measured in a powder sample prepared by grinding several small crystals, while the angular dependence was measured on a single crystal mounted on a sample rotator. The spin-lattice relaxation time T_1 was measured on the same single crystal, using the saturation-recovery method in several fields between 1.0 and 5.5 T. As expected, the nuclear magnetization recovery was found to fit a simple exponential for these $I=1/2$ nuclei, allowing us to determine a unique T_1 value at each temperature and field.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Temperature dependence of the NMR shift

The inset to Fig. 1 shows a ^{31}P NMR spectrum obtained in the powder sample. This spectrum shows a typical powder pattern with a uniaxial NMR shift distribution for nuclear spin $I=1/2$. The shift values $K_{\parallel}$ and $K_{\perp}$ parallel and perpendicular to the principal axis, respectively, were thus derived from the extremal singularities in the powder-pattern spectrum, taking broadening into account, as shown in Fig. 1. The T dependences of $K_{\parallel}$ and $K_{\perp}$ are shown in the main panel of Fig. 1.

From $K_{\parallel}$ and $K_{\perp}$, the isotropic ($K_{\rm iso}$) and anisotropic ($K_{\rm ai}$) parts of the NMR shift can be deduced using the relations $K_{\rm iso}=(K_{\parallel}+2\,K_{\perp})/3$ and $K_{\rm ai}=(K_{\parallel}-K_{\perp})/3$, respectively. As shown in the main panel of Fig. 2, the shift is seen to consist of a large anisotropic part and a small isotropic part. Both components have a similar temperature dependence to that of $\chi(T)$, i.e., they rapidly increase as T decreases below 20 K. The ratio of the shift components $K_{\rm ai}/K_{\rm iso}$ is $\sim$2.5 at high temperature and $\sim$4 at low temperature near T_C. The rela-

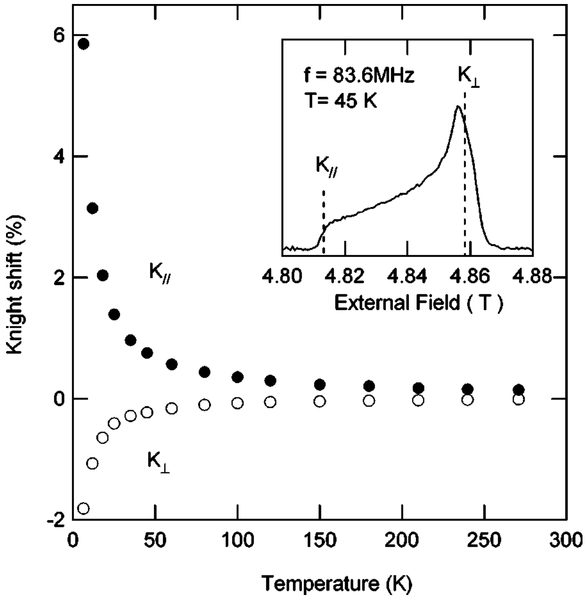

FIG. 1. Temperature dependence of the NMR shift with the field both parallel and perpendicular to the principal axis of the shift tensor. The inset shows the NMR spectrum in a powder sample of UFe_4P_{12} at 45 K.

tively small isotropic term in the NMR shift suggests a rather small conduction electron contribution in the ^{31}P hyperfine (HF) mechanism.

The inset to Fig. 2 shows a plot of $K_{\mathrm{iso,ai}}$ vs χ with temperature as an implicit parameter. Both K_{iso} and K_{ai} maintain a linear relation with $\chi(T)$, except for a small deviation in the temperature region below 20 K. The slopes of the K-χ plots yield for the HF coupling constants A_{ai} and A_{iso} the values 1180 and 315 Oe/μ_B, respectively. It should be noted that these values are both much larger than the values $A_{\mathrm{ai}} = 139$ Oe/μ_B and $A_{\mathrm{iso}} = 137$ Oe/μ_B obtained for the isostructural compound $PrFe_4P_{12}$ from ^{31}P-NMR measurements.[10] The sharp contrast in HF couplings between these compounds suggests a strong hybridization between P and U orbitals in UFe_4P_{12}. This may be related to the relatively large CEF splitting suggested from specific heat, magnetic susceptibility and high-field magnetization measurements.[9]

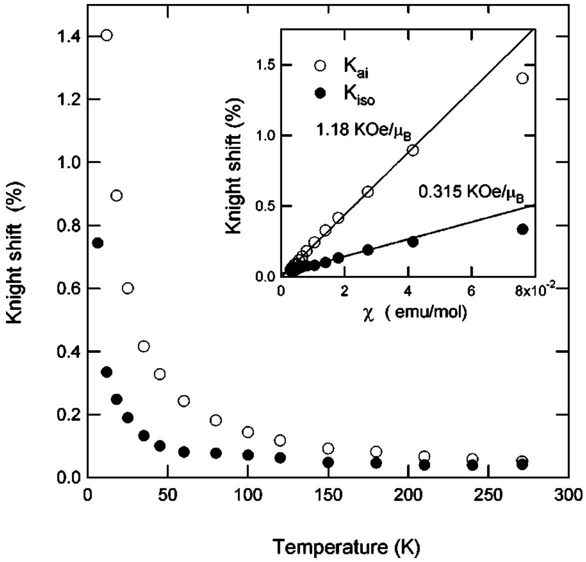

FIG. 2. Temperature dependence of the anisotropic (K_{ai}) and isotropic (K_{iso}) terms of the NMR shift. In the inset, K_{ai} and K_{iso} are plotted against the bulk susceptibility χ with temperature as an implicit parameter. The slopes of the solid lines correspond to anisotropic and isotropic HF coupling constants A_{ai} and A_{iso} of 1.18 kOe/μ_B and 315 Oe/μ_B, respectively.

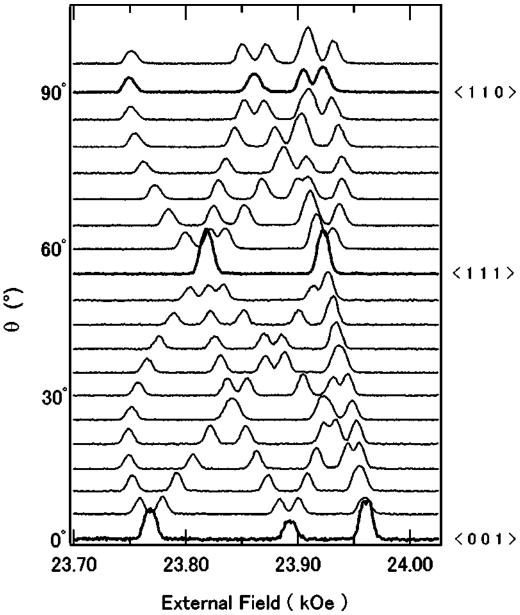

FIG. 3. The angular dependence of the ^{31}P NMR spectrum in a single crystal taken at 50 K and 2.4 T. θ indicates the angle of tilt for the field as it rotates from ⟨001⟩ to ⟨110⟩ through the ⟨111⟩ directions of the UFe_4P_{12} crystal.

B. Angular dependence of the hyperfine fields

In the paramagnetic state, the susceptibility χ of UFe_4P_{12} is found to be isotropic. Therefore, the anisotropic term in the NMR shift indicates that the HF coupling mechanism itself is anisotropic. In order to obtain further insight into the HF mechanism in UFe_4P_{12}, the angular dependence of the ^{31}P NMR shift has been measured using a single crystal. Results obtained at 50 K in an external field of 2.4 T are shown in Fig. 3, where θ is the tilting field angle from ⟨001⟩ to ⟨110⟩ through the ⟨111⟩ directions for the cubic crystal axis. The NMR line splits into several peaks, and these peaks change position with sample rotation. The angular dependence of the peak position, corresponding to the angular dependence of the HF field at the P nuclei, is shown in the upper panel of Fig. 4. We have obtained a series of six curves merging into four, three, and then two at the ⟨110⟩, ⟨001⟩, and ⟨111⟩ directions, respectively. Note that the angle-dependent NMR line splitting is of purely magnetic origin, since the ^{31}P nuclei ($I = 1/2$) have no electric quadrupole moment. The observed line splittings are due to anisotropic HF effects at the P sites.

In the filled skutterudite structure there are twelve crystallographically equivalent P sites in the cubic unit cell. How-

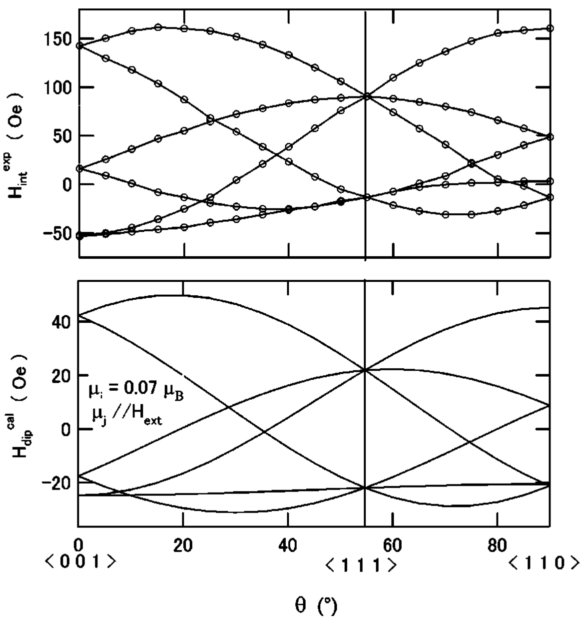

FIG. 4. The upper panel shows the angular dependence of the internal field at P sites deduced from the NMR spectrum peak positions in Fig. 3. The lower panel shows the angular dependence of the direct dipolar field calculated for twelve P sites assuming localized moments of $\overline{\mu_j}=0.07\mu_B$ along the field direction located on the U sites.

ever, the local symmetry at P sites is lower than cubic, and the directions of the local symmetry axes of the P sites are all different. These axes are classified into six inequivalent directions in an external field. The NMR line splittings in the single crystal correspond to a distribution of HF fields over these P sites. On the other hand, in the powder sample grains are randomly oriented, and thus the field effect is averaged over all directions. Consequently, a powder pattern spectrum corresponding to a single P site is obtained with the powder sample, as seen in the inset to Fig. 1.

When the symmetry at the nucleus is lower than cubic, the dipolar interaction gives rise to an anisotropic HF coupling. Let us first consider the dipolar coupling between U-5f electrons and ^{31}P nuclei. Assuming the 5f electrons to be localized at the U sites in UFe$_4$P$_{12}$, the direct dipolar field from the U spin moments at site j to the ^{31}P nucleus at site i is given by

$$H_{\mathrm{dip}}^{ij}=\left[3\frac{\overline{\mu_j}\cdot\vec{r}_{ij}}{r_{ij}^5}-\frac{\overline{\mu_j}}{r_{ij}^3}\right], \tag{1}$$

where $\overline{\mu_j}$ is the time average 5f spin moment along H_{ext}. Using Eq. (1), the direct dipolar field at a ^{31}P site is obtained by summing over all of the U moments in the crystal.

The lower panel of Fig. 4 shows the angular dependence of H_{dip} calculated for the twelve P sites in the unit cell. In this calculation, we adopt $\overline{\mu_j}=0.07\mu_B$, which is obtained from magnetization measurements at $T=50$ K and $H=2.4$ T. A series of six curves with a θ dependence similar to the experiment have been obtained. The agreement seen between calculated and experimental behavior confirms the full filling of U atoms in our single crystal as well as the absence of large magnetic moments on the Fe sites. Quantitatively, however, the present point-dipolar calculations are clearly rather smaller than the total anisotropic HF fields observed at the P sites, giving only about one third of the magnitude of the experimental values shown in Fig. 4. This suggests that another HF mechanism, i.e., the hybridization of the U spin moment into p orbitals on the P sites, has a magnitude similar to the direct dipolar mechanism. Moreover, from the agreement between the calculated and experimental results in Fig. 4, it is seen that the transferred HF mechanism (H_{tr}) also has an angular dependence similar to the direct dipolar mechanism in UFe$_4$P$_{12}$.

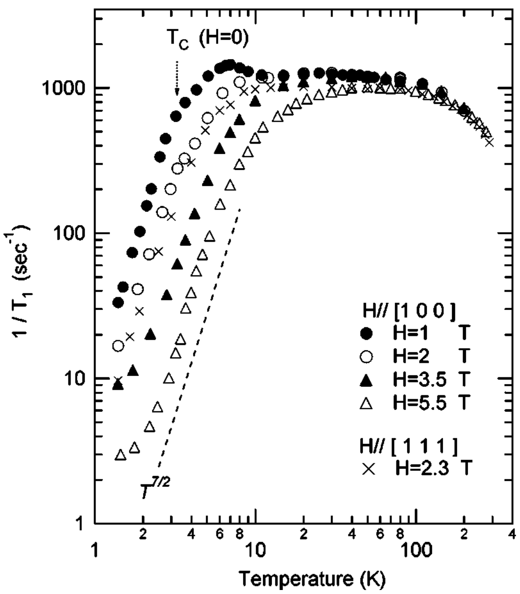

FIG. 5. The temperature dependence of $1/T_1$ measured at fields of 1, 2, 3.5, and 5.5 T(‖[1 0 0]) and 2.3 T(‖[1 1 1]), respectively.

Evaluating such a hybridization effect would require a complete solution to the quantum chemistry of the hybridization process, which is not available. For simplicity, we assume here that the anisotropic H_{tr} is mainly due to the transferred spin moment in 3p orbitals through the conventional hybridization effect. In this case, substantial HF fields at on-site P nuclei are expected to be generated by 3p spin moments through the dipolar mechanism, and thus given by a formula similar to Eq. (1). If the literature value $\langle r^{-3}\rangle_{3p}=3.48\ a_0^{-3}$ is adopted for P atoms, we estimate that roughly 1% of μ_j at a 3p orbital is enough to produce H_{tr} of the same order of magnitude as H_{dip} in UFe$_4$P$_{12}$.

C. The spin-lattice relaxation time T_1

The spin-lattice relaxation time T_1 has been measured in our single-crystal sample with the applied field parallel to the [100] direction. Figure 5 shows the temperature dependence of $1/T_1$ measured in fields of 1, 2, 3.5, and 5.5 T. The data show a flat behavior in the midrange of temperature with a slight decline at the upper end and a steep drop at the low end of the range. For the lowest field $H=1$ T there is a broad peak just above T_C indicative of critical slowing down of U moment fluctuations. With increasing magnetic field, any

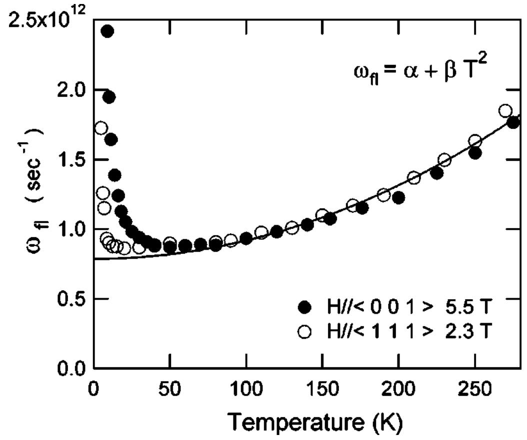

FIG. 6. The temperature dependence of $T_1 \propto \omega_{fl}(T)$. The solid line shows the relation $\omega_{fl}(T) \sim \alpha + \beta T^2$.

such divergence in $1/T_1$ is rapidly suppressed, and $1/T_1$ starts to decrease from far above T_C. The anomaly related with the onset of ferromagnetic ordering is no longer distinguishable in high magnetic field. A similar decrease of $1/T_1$ at low temperature is also observed with the field applied parallel to the [111] directions, as shown in Fig. 5.

For nuclear spin relaxation driven by fluctuating local moments, $1/T_1$ may be expressed as[12]

$$1/T_1 = \sqrt{2\pi}(g\gamma_N)^2 A_{\mathrm{hf}}^2 \frac{J(J+1)}{3\omega_{\mathrm{fl}}}, \tag{2}$$

where ω_{fl} is the local moment fluctuation rate, assumed $\gg \gamma H$. In general, ω_{fl} is given by two major processes, i.e., ω_{ex} and ω_{cf}. The ω_{ex} process is caused by exchange interactions among local moments and the ω_{cf} process is due to the spin exchange interaction with conduction electrons. The former is given by $\omega_{\mathrm{ex}}^2 = 8zJ_{\mathrm{ex}}^2[J(J+1)]/(3\hbar^2)$, and the latter by $\omega_{\mathrm{cf}} = (\pi)(\hbar)(J_{\mathrm{cf}}\rho)^2 k_B T$. Here, J_{ex} is the superexchange coupling between U moments, J_{cf} is the spin exchange coupling between the U local moments and conduction electrons, ρ is the band density of states, and z is the number of nearest-neighbor moments, i.e., $z=8$ in our case. Note that the former gives a T-independent T_1, while the latter gives a T-dependent T_1 process. In $\mathrm{UFe_4P_{12}}$, a T-independent T_1 is observed at lower fields between 10 and 100 K. In this case, it is suggested that the dominant interaction for the U local moments is their mutual superexchange coupling J_{ex}, which finally mediates ferromagnetic order below T_C. From the constant value of $1/T_1 \sim 1.2 \times 10^3$ s^{-1} with the Eq. (2) and $\mu_{\mathrm{eff}} = 3.0\mu_B$, J_{ex}/k_B is estimated to be ~ 0.29 K, which is agrees in order of magnitude with $J_{\mathrm{ex}}^*/k_B \sim 0.1$ K expected from mean-field theory for $T_C = 3.15$ K.

At higher temperatures, however, $1/T_1$ shows a decrease above 100 K, which is not expected with the ω_{ex} process alone. From Eq. (2), the decrease of $1/T_1$ is presumably related with an increase in ω_{fl}, suggesting that another U-moment relaxation process sets in at higher temperature. The T dependence of ω_{fl} ($\propto T_1$) in this temperature range is well fitted by $\omega_{\mathrm{fl}}(T) = \alpha + \beta T^2$, as shown in Fig. 6. Similar $\omega_{\mathrm{fl}} \propto T^2$ behavior has been found in $\mathrm{PrOs_4Sb_{12}}$ above 40 K.[10,11] A possible origin of the ω_{fl} at high temperature is due to the ω_{cf} process associated with conduction electrons. However, the ω_{cf} process usually gives a T-linear T_1 as mentioned earlier. Furthermore, if the ω_{cf} process is viable, then $R(T) \propto -\ln T$ behavior via the interaction of $J_{\mathrm{cf}}\rho$ is also expected for resistivity measurements in the same temperature region. This, however, is not observed in insulating $\mathrm{UFe_4P_{12}}$. Another scenario is scattering due to thermal phonon excitations of the P cages which surround the U ions. This phonon relaxation process was proposed by Ishida *et al.* to explain the T^2 behavior for ω_{fl} observed in $\mathrm{PrOs_4Sb_{12}}$.[10] In filled skutterudites, the presence of a incoherent localized vibrational mode originating from the "rattling" of the filling atom has been reported.[13,14] Ishida *et al.* has suggested that these fluctuations of the electric-field gradient at Pr sites would lead to localized $4f$ moment fluctuations through the coupling between J and the quadrupole moments Q associated with the Pr-$4f$ orbitals. In this case, $\omega_{\mathrm{fl}} \propto T^2$ is expected, in analogy with the well-known the phonon-Raman nuclear quadrupole relaxation process. The same scenario may be applicable to the U-$5f$ case to explain the apparent T^2 term in $\omega_{\mathrm{fl}}(T)$ mentioned above for $\mathrm{UFe_4P_{12}}$.

Finally, we comment on the strong temperature and field dependence for $1/T_1$ at low temperature. This behavior is typical for magnetic insulators. Similar $1/T_1$ behavior has been reported in several ferromagnetic insulators, such as EuO ($T_C = 69.4$ K) (Ref. 15) and EuS ($T_C = 16.5$ K).[16] In these compounds, the nuclear relaxation at temperatures well below T_C was analyzed using the multimagnon scattering theory. The suppression of $1/T_1$ was interpreted as due to an increase in the energy gap of the magnon excitation spectrum by the applied field.

In the ferromagnetic case, if the HF interaction is anisotropic, a two-magnon Raman process and a three-magnon process are suggested to induce nuclear spin flips, and thereby, spin-lattice relaxation.[17,18] These two processes are distinguished most clearly by their contrasting temperature dependences $1/T_1 \propto T^2$ for the former and $\propto T^{7/2}$ for the latter. In $\mathrm{UFe_4P_{12}}$, we found that $1/T_1$ shows approximately $T^{7/2}$ behavior at low temperatures, as shown in Fig. 5. Therefore, it seems that the three-magnon processes are dominant for nuclear relaxation in $\mathrm{UFe_4P_{12}}$. However, the lowest temperature in our experiment is 1.4 K, which is not very low compared with $T_C = 3.15$ K in $\mathrm{UFe_4P_{12}}$. Further experimental effort may be needed at lower temperatures to clarify this point. We are also planning to perform a direct ^{235}U NMR study in the ferromagnetic ordered state using a ^{235}U-enriched $\mathrm{UFe_4P_{12}}$ sample.

IV. SUMMARY

^{31}P NMR measurements have been performed on the uranium-based ferromagnetic insulator $\mathrm{UFe_4P_{12}}$ with $T_C = 3.15$ K. The HF coupling between the $5f$ electrons and the ^{31}P nuclei has been found to be much larger than that reported for $\mathrm{PrFe_4P_{12}}$, indicative of stronger hybridization between U-$5f$ and P-$3p$ orbitals. On the other hand, the magnetic properties of $\mathrm{UFe_4P_{12}}$ seems to be rather simple compared with the case of $PrFe_4P_{12}$. The T-independent T_1 in the paramagnetic state as well as the T_1 decrease in the ferromagnetic region are explained by a localized picture of U-5f electron excitations. Although additional work is clearly needed to have a complete understanding of the electronic state of UFe_4P_{12}, we believe that the rather simple magnetic properties are largely due to the localized character of U 5f electrons. It seems unlikely to consider that the insulating behavior arises from strong f-electron hybridization effects as in a Kondo insulator. High-temperature behavior in which $T_1 \propto T^2$, which had previously been reported for $PrOs_4Sb_{12}$ has also been found in the present study of UFe_4P_{12}.

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