$^{235}$U nuclear relaxation rates in an itinerant antiferromagnet USb$_2$

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(Received 9 November 2009; published 23 February 2010)

$^{235}$U nuclear spin-lattice ($T_1^{-1}$) and spin-spin ($T_2^{-1}$) relaxation rates in the itinerant antiferromagnet USb$_2$ are reported as a function of temperature in zero field. The heating effect from the intense rf pulses that are necessary for the $^{235}$U NMR results in unusual complex thermal recovery of the nuclear magnetization which does not allow measuring $T_1^{-1}$ directly. By implementing an indirect method, however, we successfully extracted $T_1^{-1}$ of the $^{235}$U. We find that the temperature dependence of $T_1^{-1}$ for both $^{235}$U and $^{121}$Sb follows the power law ($\propto T^n$) with the small exponent $n=0.3$ suggesting that the same relaxation mechanism dominates the on-site and the ligand nuclei, but an anomaly at 5 K was observed, possibly due to the change in the transferred hyperfine coupling on the Sb site.

DOI: 10.1103/PhysRevB.81.054435

PACS number(s): 76.60.–k, 71.27.+a

I. INTRODUCTION

In actinide-based materials, $5f$ electrons often exhibit itinerant and localized behaviors simultaneously, which is in contrast to the usually localized $4f$ electrons in the rare-earth compounds. The unique nature of the $5f$ electrons has been known to be the origin of various unusual physical properties found in actinide-based materials such as unconventional superconductivity, non-Fermi-liquid behavior, and multipoar ordering. However, since the degree of the $5f$ localization is highly sensitive to the specific ligand atoms and the crystal structure, the nature of $5f$ electrons is not easily elucidated even in a single compound.

In principle, nuclear magnetic resonance (NMR) is an ideal method to investigate $5f$ electrons by probing on-site actinide nuclei ($^{235}$U, $^{237}$Np, $^{239}$Pu) since they are directly influenced by $5f$ electrons both dynamically and statically. However, NMR in the actinide nuclei is extremely difficult. For $^{235}$U, for instance, the tiny nuclear gyromagnetic ratio $\gamma_n=0.784$ MHz/T and very low natural abundance (0.72%) present significant challenges for detecting the NMR. Furthermore, the fast spin fluctuations of the $5f$ electrons require an ordered state in which the spin fluctuations are sufficiently suppressed to allow the detection of NMR signal. Despite these difficulties, $^{235}$U NMR was successfully carried out recently in an insulating UO$_2$ and an itinerant USb$_2$ in their antiferromagnetically ordered states. While $^{235}$U nuclear relaxation rates were measured in detail in UO$_2$, these quantities were not measured in USb$_2$ that is highly itinerant. Motivated by the absence of $T_1^{-1}$ in metallic U-based materials, we investigated the $^{235}$U nuclear relaxation rates in USb$_2$.

USb$_2$ is a member of the uranium dipnictides, UX$_2$ family ($X=\text{P, As, Sb, Bi}$), which is characterized by strong magnetic and electronic anisotropies, and the hybridization of the $5f$ electrons with the conduction electrons. USb$_2$ crystallizes in the tetragonal Cu$_2$Sb$_2$-type structure (space group: $P4/nmm$) and undergoes antiferromagnetic transition at $T_N=203$ K with an ordered moment of $1.88\mu_B$. The magnetic unit cell is doubled along the $c$ axis with respect to the chemical unit cell due to the sequence of alternating ferromagnetic layers ($\uparrow\downarrow\downarrow\uparrow$), as depicted in Fig. 1. dHvA experiment$^8$ detected the two-dimensional Fermi surfaces which are in agreement with the band calculations$^6$ and the dual nature of the $5f$ electrons was confirmed by angle resolved photoemission spectroscopy (ARPES) study$^9$ from very narrow strongly dispersive bands at the Fermi level with $5f$ character. In this paper, we report the $^{235}$U nuclear spin-

![Graphical representation of the crystallographic and magnetic structure of USb$_2$. Arrows indicate the direction of the ordered moments along the c axis. Ferromagnetic planes are coupled ferromagnetically through Sb(I) plane but antiferromagnetically through Sb(II) plane.](attachment:Graphical_representation.png)
lattice ($T_1^{-1}$) and spin-spin ($T_2^{-1}$) relaxation rates in $^{235}$U-enriched USb$_2$.

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

We have grown single crystals of USb$_2$ enriched with $^{235}$U (93.5% enrichment) using flux growth in excess Sb. The $^{235}$U was arc-melted prior to the flux growth to remove the high vapor-pressure daughters, radium, in particular. Most of the USb$_2$ produced was in the form of a single crystal weighing approximately 340 mg. Because the rf penetration depth is small an increase in signal strength can be accomplished by powdering the sample. The crystal was broken into pieces and ~100 mg of material was ground into powder using an agate mortar and pestle. A pickup coil with an inside diameter of ~2 mm was cast into an epoxy block and after curing a cylindrical sample space was drilled into the epoxy within the inner diameter (ID) of the pickup coil. A 2 μm pore size stainless steel frit was glued over one end of the sample space. The USb$_2$ powder was funneled into the open end of the sample space and a then a second frit glued on to close the open end. The frits allow thermal contact of the powder with the cryogenic fluid/gas and prevent the radioactive material from spreading into the apparatus.

$^{235}$U and $^{121}$Sb NMR were performed in zero field in the temperature range 1.5–80 K. The NMR spectra were obtained by integrating averaged spin-echo signals as a function of frequency and the spin-lattice relaxation rates ($T_1^{-1}$) were measured by acquiring Hahn echoes following various delays after a saturation pulse, i.e., $\pi/2-t-\pi/2-\tau-\pi$, where $t$ represents the variable delay, $\pi/2$ pulse was about 10 μs, and the repetition time longer than 1 s was used to reduce the heating effect. In order to extract $T_1$, we fit the raw data with the appropriate relaxation functions. The value of the nuclear spin-spin relaxation rate ($T_2^{-1}$) was obtained by monitoring the spin-echo amplitude, $M(2\tau)$, as a function of $2\tau$ between the first pulse and the echo. The $M(2\tau)$ were fitted to an exponential decay curve $M(0)\exp(-2\tau/T_2)$.

III. EXPERIMENTAL RESULTS AND DISCUSSION

From the detailed spectra of $^{121,123}$Sb and $^{235}$U given in Ref. 2, we were able to confirm $^{235}$U signal at 217.4 MHz and the second satellite transition ($5/2\rightarrow3/2$) of $^{121}$Sb(I) at 229 MHz as shown in Figs. 1(a) and 1(b). While $^{121}$Sb spectrum has a Lorentzian shape, the U spectrum is asymmetric with shoulders in low-frequency side. Since there is only one U-crystallographic site in the unit cell, we suggest that a transferred hyperfine coupling from nearest-neighbor U sites may lead to different inequivalent U sites in the complex magnetic structure. Indeed, the alternating ferromagnetic U planes suggest that different transferred hyperfine coupling may result from the different interlayer magnetic interactions either through Sb(I) plane or Sb(II) plane. We will not present further analysis of this complicated $^{235}$U spectrum in this paper and, instead, we focus on the nuclear relaxation rates of $^{235}$U, which have never been directly measured in an itinerant magnetic material.

FIG. 2. (Color online) Recovery of nuclear magnetization $M(t)$ as a function of time $t$ with varying temperature $T$. $M(t)$ shows an oscillating behavior with varying $t$, forming a local minimum near $t=5$ ms. For $t<1$ ms, $M(t)$ is almost independent of $T$ while the local minimum becomes deeper with decreasing temperature maintaining the same position in time. Inset: for comparison, the recovery curves for $^{121}$Sb are shown.

A. Thermal recovery of $^{235}$U nuclear magnetization

As we try to measure $^{235}$U, it turns out that the recovery of the nuclear magnetization, $M(t)$, is very unusual as shown in Fig. 2. With our experimental conditions, we were unable to make the full saturation of the line and there are always sizable signal more than 20% with regard to the full amplitude. Also $M(t)$ as a function of temperature $T$ does not change below $t<0.5$ ms but it reveals an oscillating behavior with the minimum near $t=5$ ms. With decreasing $T$, the minimum becomes deeper without the change in its position in $t$.

We speculate that the unusual behavior of $M(t)$ is due to the strong rf pulse in the sample coil, which may produce considerable heat causing complex thermal recovery of the nuclear magnetization. To flip a nuclear spin, we apply a $\pi/2$ pulse that satisfies the relation $\gamma_H t \tau = \pi/2$, where $H$ corresponds to the rf strength (power) and $\tau$ the duration of the pulse. Since $\gamma_H=0.784$ MHz/T of $^{235}$U is one order of magnitude smaller than typical nuclei (e.g., 10.189 MHz/T for $^{121}$Sb), the total energy transferred to the coil, $H_1 \tau$, should be large correspondingly. Moreover, the cooling power is substantially reduced in the measurement since the sample is located inside an epoxy block to prevent the contamination. Thus, the heating effect may be a consequence from the experimental limitations with regard to the $^{235}$U nuclei.

In order to account for the heating effect, we measured two data sets with different experimental conditions. One is measured through the usual sequence for measuring $T_1$. In an other sequence, we apply the saturating $\pi/2$ pulse at off-resonance frequency $\omega_{0f}$ as depicted in the inset of Fig. 3(a). The detecting pulses consisting of $\pi/2-\pi$ are the same in
We treat \( M(t)_{\text{therm}} \) as the fully recovered constant value \( M_0 \) at each time so that the nuclear relaxation function can be written as

\[
R(t) = 1 - M(t)_{\text{tot}}/M(t)_{\text{therm}}.
\]

This accounts for not only the heating effect inside the sample coil but also any possible artificial effect originating from the power amplifier or the receiver. The corrected relaxation data are shown in Fig. 3(b) and we fit the data with the relaxation function for the central transition of \( I=7/2 \) (solid lines)

\[
R(t) = \frac{1}{84} \exp\left(-\frac{t}{T_1}\right) + \frac{3}{44} \exp\left(-\frac{6t}{T_1}\right) + \frac{75}{364} \exp\left(-\frac{15t}{T_1}\right) + \frac{1225}{1716} \exp\left(-\frac{28t}{T_1}\right).
\]

Here we assume a large quadrupole frequency \( \nu_q \) which is estimated to be \( \sim 140 \text{ MHz} \) from Mössbauer spectroscopy\(^\text{10}\) so that the rf irradiation induces the central transition only. Also we expect that the spectral diffusion, if any, does not affect the obtained \( T_1 \) values since it should occur at times that are much shorter than \( T_1 \). Note that the correct scaling behavior in \( T_1^{-1} \) between \(^{121}\text{Sb} \) and \(^{235}\text{U} \) in Eq. (4), as discussed below, supports the validity of Eq. (2).

\section*{B. Nuclear relaxation rates, \( T_1^{-1} \) and \( T_2^{-1} \)}

The \(^{235}\text{U} \) nuclear spin-lattice relaxation rate \( 235 T_1^{-1} \) as a function of temperature is shown in Fig. 4(a). The data can be fit by a power law \( T_1^{-3} \) in the measured temperature range. \(^{121}\text{Sb} \) nuclear spin-lattice relaxation rate \( 121 T_1^{-1} \) also shows the same power law behavior with a factor of four smaller prefactor than that of \( 235 T_1^{-1} \). In general, \( T_1^{-1} \) due to the spin fluctuations is given by\(^\text{11}\)

\[
T_1^{-1} \approx 2 T_r^2 A_{hf}^2 \frac{\sum \chi''_\perp(q, \omega_0)}{\omega_0},
\]

where \( A_{hf} \) is the hyperfine coupling constant at \( q=0 \), \( \chi''_\perp \) is the imaginary part of the \( q \)-dependent dynamic susceptibility at the nuclear Larmor frequency \( \omega_0 \) that represents the spin fluctuations in the perpendicular plane. Since \( \sum \chi''_\perp(q, \omega_0) \) should be the same for both nuclei, the following relation should hold:

\[
\frac{235 T_1^{-1}}{121 T_1^{-1}} \approx \left( \frac{A_{hf}^{121}}{A_{hf}^{235}} \right)^2.
\]

where \( A_{hf} \) is 5.69 T/\( \mu_B \) for \(^{121}\text{Sb} \) and 147.5 T/\( \mu_B \) for \(^{235}\text{U} \).\(^\text{2} \) Indeed, the experimental values \( 235 T_1^{-1} \) and \( 121 T_1^{-1} \) are well scaled according to Eq. (4) above 5 K as shown in the inset of Fig. 4(a). The slight difference between the two data may be due to systematic error from to the indirect way of acquiring \( 235 T_1^{-1} \). However, we find that \( 235 T_1^{-1} \) and \( 121 T_1^{-1} \) data are also scaled with the same ratio between the two \( T_1^{-1} \) data sets at high temperatures. This suggests that the spin fluctuations dominate both \( T_1^{-1} \) and \( T_2^{-1} \) for the two nuclei. Since both \( T_1^{-1} \) and \( T_2^{-1} \) are scaled with the same ratio, we argue that the slight difference in \( \sum \chi''_\perp(q, \omega_0) \) may be attributed to an additional contribution to the relaxation rates other than the spin fluctuations, probably, due to the lattice vibrations (phonons) which are not necessarily the same for both nuclei.
For temperatures larger than about 5 K, $T_1^{-1}$ of both nuclei decreases slowly with decreasing temperature, revealing the $T^{0.3}$ power-law behavior. Below 5 K, however, $121T_1^{-1}$ changes abruptly and varies linearly with temperature, yet $235T_1^{-1}$ shows no change down to 1.5 K. A similar deviation in the temperature dependence of $T_2^{-1}$ is observed at 5 K, as shown in Fig. 4(b). Namely, $121T_2^{-1}$ increases rapidly but $235T_2^{-1}$ increases slightly and saturates, with decreasing $T$. Interestingly, for U, both nuclear relaxation rates change somewhat with temperature, but for the Sb, $T_1^{-1}$ decreases and $T_2^{-1}$ increases below $\sim$5 K resulting in the fast increase in the ratio $T_2^{-1}/T_1^{-1}$ with decreasing $T$.

In the ordered antiferromagnetic state, $T_1^{-1}$ is usually dominated by the fluctuations of the magnetic structure (magnons), in which a two magnon Raman process yields $T_2^{-1}$ behavior. Thus, the very small exponent of 0.3 in our case suggests that the relaxation mechanism in USb$_2$ is not governed by the simple magnon process. Although the origin of $T^{0.3}$ behavior is not clear, it suggests that the same relaxation mechanism is applicable to both on-site and ligand nuclear sites.

The clear anomaly of both $121T_1^{-1}$ and $121T_2^{-1}$ at 5 K in contrast to those of $235U$ implies the dramatic change in the hyperfine coupling mechanism for $121Sb$. Since $A_{hf}$ for $235U$ is expected to be isotropic due to the overwhelming on-site Fermi contact term which is isotropic, the anisotropy of the spin fluctuations above $\sim$5 K may be estimated using Eqs. (3) and (5), i.e., $\sum_q \rho_2(q)/\sum_q \rho_1(q) \sim 18$. When this ratio is applied for $121Sb$, we obtain $A_{hf}/A_{hf} \sim 1$. Therefore, $A_{hf}$ is also apparently isotropic for $121Sb$ above 5 K. Since the anisotropy of the spin fluctuations does not change much for the $235U$, the anomaly of the relaxation rates of the $121Sb$ indicates that the anisotropy of $A_{hf}$ is developed below 5 K and the ratio $A_{hf}/A_{hf}$ increases with decreasing temperature up to 4 at 1.5 K. The anomalous behavior below 5 K may suggest that the hyperfine coupling on the Sb is very sensitive to even a small change in the electronic environment. The otherwise slight increase in $235T_2^{-1}$ below 5 K is then attributed to the cross relaxation between $235U$ and $121Sb$.

**IV. SUMMARY AND CONCLUSION**

The nuclear relaxation rates $T_1^{-1}$ and $T_2^{-1}$ of $235U$ are reported in the itinerant $5f$ electron system USb$_2$. The strong heating effect associated with the tiny gyromagnetic ratio of $235U$ prevents the direct measurement of $235T_1^{-1}$ but we successfully accounted for the heating effect using two pulse sequences. The resultant $235T_1^{-1}$ data as a function of temperature correctly scale according to $(\gamma_p A_{hf})^2$ with those of $121Sb$ and vary as $T^{0.3}$. We find that $121T_1^{-1}$ and $121T_2^{-1}$ change dramatically at $\sim$5 K while $235T_1^{-1}$ shows no change in the temperature dependence with the slight increase in $235T_2^{-1}$. The different behavior is attributed to the different hyperfine coupling mechanism but the origin of the anomaly at $\sim$5 K is not clear at present. Nevertheless, the successful direct measurement of $T_1^{-1}$ on the $235U$ in an itinerant compound will pave the way for further direct investigations of the $235U$ nuclei in other U-based compounds.
ACKNOWLEDGMENTS

We thank the useful and delightful discussions with S. Kambe and H. Kato. This work was performed at Los Alamos National Laboratory under the auspices of the U.S. Department of Energy, Office of Science, and supported in part by the Laboratory Directed Research and Development program.

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