235U nuclear relaxation rates in an itinerant antiferromagnet USb2

S.-H. Baek,1 N. J. Curro,2 H. Sakai,1,3 E. D. Bauer,1 J. C. Cooley,1 and J. L. Smith1
1Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA
2Department of Physics, University of California, Davis, California 95616, USA
3Advanced Science Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan
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235U nuclear spin-lattice (T1) and spin-spin (T2) relaxation rates were measured in detail in UO2, these quantities are necessary for the 235U NMR results in unusual complex thermal recovery of the nuclear magnetization which does not allow measuring T1 directly. By implementing an indirect method, however, we successfully extracted T1 of the 235U. We find that the temperature dependence of T1 for both 235U and 121Sb follows the power law (\(\sim T^n\)) 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.

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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 multipolar 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 (235U, 237Np, 239Pu) since they are directly influenced by 5f electrons both dynamically and statically. However, NMR in the actinide nuclei is extremely difficult. For 235U, 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, 235U NMR was successfully carried out recently1,2 in an insulating UO2 and an itinerant USb2 in their antiferromagnetically ordered states. While 235U nuclear relaxation rates were measured in detail in UO2, these quantities were not measured in USb2 that is highly itinerant. Motivated by the absence of T1 in metallic U-based materials, we investigated the 235U nuclear relaxation rates in USb2.

USb2 is a member of the uranium dipnictides, UX2 family (X=P, As, Sb, Bi), which is characterized by strong magnetic and electronic anisotropies, and the hybridization of the 5f electrons with the conduction electrons.3-6 USb2 crystallizes in the tetragonal Cu2Sb-type structure (space group: P4/nmm) and undergoes antiferromagnetic transition at TN =203 K with an ordered moment of 1.88\(\mu_B\).7 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 (\(↑\downarrow\downarrow\downarrow↑\)), as depicted in Fig. 1. dHvA experiment8 detected the two-dimensional Fermi surfaces which are in agreement with the band calculations6 and the dual nature of the 5f electrons was confirmed by angle resolved photoemission spectroscopy (ARPES) study9 from very narrow strongly dispersive bands at the Fermi level with 5f character. In this paper, we report the 235U nuclear spin-
lattice \((T_1^{-1})\) and spin-spin \((T_2^{-1})\) relaxation rates in 
\(^{235}\text{U}\)-enriched \(\text{USb}_2\).

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

We have grown single crystals of \(\text{USb}_2\) enriched with 
\(^{235}\text{U}\) (93.5% enrichment) using flux growth in excess Sb. 
The \(^{235}\text{U}\) was arc-melted prior to the flux growth to remove 
the high vapor-pressure daughters, radium, in particular. 
Most of the \(\text{USb}_2\) 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 \(\sim 100\text{ mg}\) of material was ground into 
powder using an agate mortar and pestle. A pickup coil with 
an inside diameter of \(\sim 2\text{ mm}\) 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 \(2\mu\text{m}\) pore size stainless steel frit was glued over one end 
of the sample space. The \(\text{USb}_2\) 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. 

\(^{235}\text{U}\) and \(^{121}\text{Sb}\) 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 
field strength 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 \(\mu\text{s}\), 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 \(^{121,123}\text{Sb}\) and \(^{235}\text{U}\) given in 
Ref. 2, we were able to confirm \(^{235}\text{U}\) signal at 217.4 MHz 
and the second satellite transition \((5/2\rightarrow3/2)\) of \(^{121}\text{Sb}(I)\) at 
229 MHz as shown in Figs. 1(a) and 1(b). While \(^{121}\text{Sb}\) 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 
crystalline structure. Indeed, the alternating ferromagnetic U 
planes suggest that different transferred hyperfine multiplet 
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 \(^{235}\text{U}\) spectrum in 
this paper and, instead, we focus on the nuclear relaxation 
rates of \(^{235}\text{U}\), which have never been directly measured in an 
itinerant magnetic material.
both sequences. Here, the \( Q \) factor of the tank circuit is ensured to be low enough to cover \( \omega_{\text{off}} \). So that the rf power applied at \( \omega_{\text{off}} \), \( (\pi/2)_{\text{off}} \) is fully transferred to the sample coil producing the similar amount of heat as the rf pulse applied at the resonance frequency \( \omega_{\text{on}} \). If there is no heating effect, the second pulse sequence with \( (\pi/2)_{\text{off}} \) should give rise to a constant magnetization \( M(t) = M_0 \) since the \( (\pi/2)_{\text{off}} \) pulse does not flip the nuclei. Using this procedure, the thermal recovery of the magnetization \( M(t)_{\text{therm}} \) oscillates in a similar fashion with the total recovery of the magnetization \( M(t)_{\text{tot}} \) as shown in Fig. 3(a).

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)

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

Here we assume a large quadrupole frequency \( \nu_{\text{q}} \) which is estimated to be \( \sim 140 \) 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).

\[T_1^{-1} = 2T_1^r \frac{\sum \chi_n^p(q,\omega_0)}{\omega_0},\]

where \( \chi_n^p \) is the hyperfine coupling constant at \( q=0 \), \( \chi_n^p \) 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 \( \sum \chi_n^p(q,\omega_0) \) should be the same for both nuclei, the following relation should hold:

\[
T_1^{-1} = \frac{235 T_1^{-1}}{121 T_1^{-1}} = \frac{235 (\gamma_0 A_{\text{hf}})^2}{121 (\gamma_0 A_{\text{hf}}')^2},
\]

where \( A_{\text{hf}} = 5.59 \) T/\( \mu_B \) for \( ^{121}\text{Sb} \) and 147.5 T/\( \mu_B \) for \( ^{235}\text{U} \). 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 \( \sum \chi_n^p(q,\omega_0) \) 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, $121^\text{Sb}T_1^{-1}$ changes abruptly and varies linearly with temperature, yet $235^\text{U}T_1^{-1}$ 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, $121^\text{Sb}T_2^{-1}$ increases rapidly but $235^\text{U}T_2^{-1}$ 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 $T_2^{-1}$ decreases below ~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 $T_3$ 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 $121^\text{Sb}T_1^{-1}$ and $121^\text{Sb}T_2^{-1}$ at 5 K in contrast to those of $235^\text{U}$ implies the dramatic change in the hyperfine coupling mechanism for $121^\text{Sb}$. Since $A_{hf}$ for $235^\text{U}$ is expected to be isotropic due to the overwhelming on-site Fermi contact term which is isotropic, the anisotropy of the spin fluctuations above ~5 K may be estimated using Eqs. (3) and (5), i.e., $\Sigma q_k^2/\Sigma q_k^4 \sim 18$. When this ratio is applied for $121^\text{Sb}$, we obtain $A_{hf}/A_{hf} \sim 1$. Therefore, $A_{hf}$ is also apparently isotropic for $121^\text{Sb}$ above 5 K. Since the anisotropy of the spin fluctuations does not change much for the $235^\text{U}$, the anomaly of the relaxation rates of the $121^\text{Sb}$ 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 $235^\text{U}T_2^{-1}$ below 5 K is then attributed to the cross relaxation between $235^\text{U}$ and $121^\text{Sb}$.

### IV. SUMMARY AND CONCLUSION

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