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Indirect observation of ^{235}U -NMR in URh_3

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Abstract

We propose a new method for ‘indirectly’ measuring ^{235}U NMR parameters in uranium intermetallic compounds which contain ligand nuclei observable by NMR. The spin-echo decay of ^{103}Rh NMR has been measured in both ^{235}U -enriched and non-enriched URh_3 . It was found that the ^{235}U enrichment in URh_3 induces an additional Lorentzian decay process for the ^{103}Rh nuclear spin-echo decay through unlike spin–spin coupling. This cross-relaxation effect allowed us to estimate the T_1 of ^{235}U to be $T_1 T \sim 2 \text{ s K}$ in URh_3 . No such measurement has, to our knowledge, ever been reported for an actinide intermetallic compound.

1. Introduction

5f electrons give rise to many exotic phenomena, such as heavy fermions, magnetic ordering and, possibly, superconductivity in uranium intermetallic compounds. ^{235}U NMR measurements would be a direct probe of such 5f electron behaviour, and thus would be expected to be a powerful method for investigating the nature of these exotic phenomena in such f-electron systems. Up to now, however, NMR studies on uranium compounds have been performed using ligand nuclei only, such as ^{195}Pt NMR in UPt_3 [1], and $^{69,71}\text{Ga}$ NMR in UGa_3 [2], owing to the difficulties of observing the ^{235}U NMR. Up to the present time, the direct observation of ^{235}U NMR signals has only been successful for UO_2 in its antiferromagnetically ordered state below 30.8 K [3].

The difficulties of observing the NMR of ^{235}U arise from the nature of ^{235}U nuclei. The extraordinarily small nuclear gyromagnetic ratio of 0.784 MHz T^{-1} gives a relatively small Larmor frequency and signal sensitivity even in a high magnetic field. The large nuclear quadrupole moment of $4.1 \times 10^{-24} \text{ cm}^{-2}$ causes extensive broadening of spectra from only tiny crystal distortions. The low natural abundance of 0.72% and strong radioactivity are

also problems which need to be dealt with. In addition to these, it was also expected that strong hyperfine (HF) coupling with the 5f electrons may give rise to extremely short nuclear relaxation times T_1 for ^{235}U . For example, a large HF coupling constant of $145 \pm 2 \text{ T}/\mu_B$ was found from direct ^{235}U -NMR studies on UO_2 [3]. For T_1 values less than a few tens of microseconds, detection of ^{235}U NMR signals becomes quite difficult by standard pulsed NMR techniques. Therefore, experimental estimation of T_1 is also important in order to gauge the observability of direct ^{235}U NMR in uranium compounds.

In this paper, we propose a new method to estimate the T_1 of ^{235}U ($^{235}T_1$) ‘indirectly’ in uranium intermetallic compounds which contain ligand nuclei observable by NMR. Spin–spin couplings between ^{235}U and ligand nuclei play a key role in the method. Several types of cross-coupling experiment are well known, such as spin echo double resonance (SEDOR), rotating frame double resonance (RFDR) etc. Here we employ a very simple effect, where through unlike spin–spin coupling the $^{235}T_1$ -modulated ^{235}U spins contribute to the spin-echo decay (T_2) process of ligand nuclei [4]. By applying this method to URh_3 , we have estimated $^{235}T_1(T)$ to be given by $^{235}T_1 T \sim 2 \text{ s K}$. This is, to our knowledge, the first such estimate for the metallic state of a uranium compound.

2. Experimental procedure and results

Two polycrystalline samples of URh_3 were prepared using the method of arc melting, one with natural abundance uranium and the other with an enrichment of 20% ^{235}U . URh_3 has the cubic AuCu_3 structure and shows ‘wide-band’ transition metal behaviour due to the 5f orbit–ligand hybridization. A nearly T -independent (i.e., Pauli-like) susceptibility showing no magnetic transitions has been reported for the temperature range 2–300 K [5].

The ^{103}Rh NMR experiments were carried out using a conventional pulsed phase-coherent spectrometer along with a superconducting magnet with a maximum field of 9 T. The isotope ^{103}Rh ($I = 1/2$) is 100% naturally abundant and $^{103}\gamma_N = 1.340 \text{ MHz T}^{-1}$, which is nearly twice that of ^{235}U . The ^{103}Rh NMR spectrum was obtained by sweeping the magnetic field at a constant NMR frequency of 10.075 MHz. The spectra show a typical powder-pattern for a resonance with a Knight shift anisotropy of axial symmetry. All of the T_1 and T_2 measurements were taken at the field value corresponding to the peak of the spectrum.

$^{103}T_1$ was measured using the standard saturation recovery technique for both the enriched and non-enriched samples. A single saturation pulse is applied at time t before a spin-echo sequence, and the recovery of nuclear magnetization is obtained by sweeping t . $^{103}T_1$ was determined by fitting the recovery curves to a single-exponential function. The results for both samples showed Korringa-like behaviour ($^{103}T_1 T = \text{constant}$) up to 255 K. We note that the recovery curves as well as the Knight shift were found to agree precisely between the two samples, as shown in figure 1(a). This gives strong evidence that the magnetic properties of URh_3 were not affected by the ^{235}U enrichment.

Figure 1(b) shows the integrated spin-echo intensity $M(\tau)$ recorded as a function of the time τ between the excitation pulse and the refocusing pulse. In all the T_2 measurements we report, these two pulses were adjusted carefully to keep a $\pi/2$ – π condition. In the non-enriched sample, $M(\tau)$ shows a simple Gaussian decay throughout the temperature region studied, and the spin-echo decay rate was obtained by simply fitting the decay to the function $M(\tau) = A \exp[-(2\tau/T_{2G})^2]$ at each temperature. On the other hand, $M(\tau)$ in the enriched sample showed a deviation from Gaussian decay above 80 K. In this temperature range, we found that $M(\tau)$ was well fitted by the function

$$M(\tau) = B \exp[-(2\tau/T_{2G})^2 - \tau/T_{2L}], \quad (1)$$

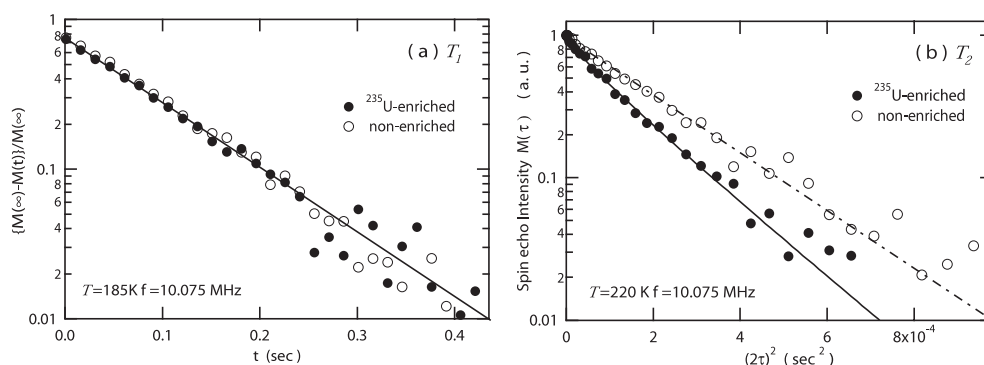


Figure 1. (a) T_1 recovery and (b) T_2 decay curves for ^{103}Rh in the ^{235}U enriched and non-enriched URh_3 . The lines show the results of fitting to (a) a single-exponential function, and to (b) a Gaussian function (dashed line) and the function of equation (1) (solid line), respectively (see the text).

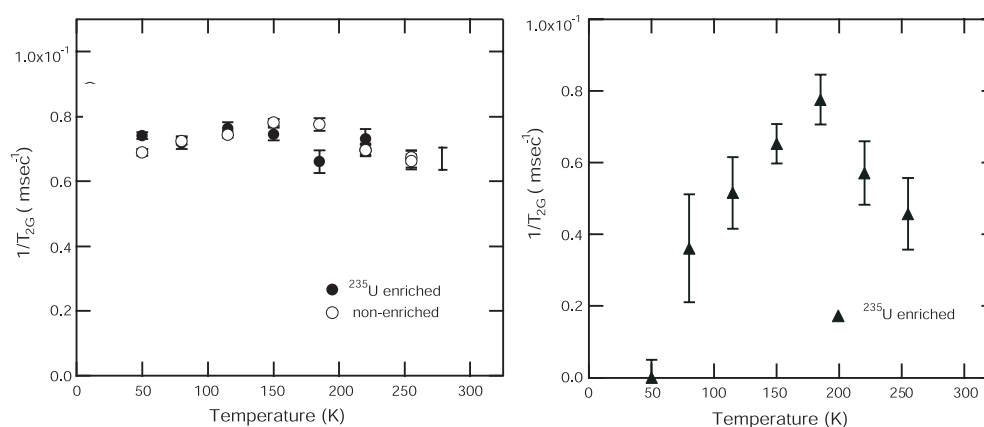


Figure 2. T dependence of $1/T_{2G}$ and $1/T_{2L}$ in the ^{235}U enriched and non-enriched URh_3 samples.

as shown in figure 1(b). Note that the data have been scaled so that A and B are essentially unity. In the enriched sample, then, two different decay rates $1/T_{2G}$ and $1/T_{2L}$ were obtained at each temperature.

The T dependences of $1/T_{2G}$ and $1/T_{2L}$ are shown in figure 2. The Gaussian decay rates $1/T_{2G}$ observed in the enriched and non-enriched samples were found to be nearly identical, even though they were extracted using different fitting functions. This result is to be expected if we notice that the T_{2G} decay process comes entirely from the like-spin second moment for the ^{103}Rh nuclei, which is, in principle, independent of the ^{235}U density in the samples. From $T_{2G} = (2/(\langle\Delta\omega^2\rangle_{AA}))^{1/2} \approx 13$ ms, the value $\langle\Delta\omega^2\rangle_{AA} \approx 1.2 \times 10^4 \text{ s}^{-2}$ is obtained for the like-spin second moment. On the other hand, the Lorentzian decay component $1/T_{2L}$ is only observed in the enriched sample. $1/T_{2L}$ shows a strong T dependence with a significant peak around 180 K. The origin and expected behaviour of $1/T_{2L}$ will be discussed in the next section.

3. Discussion

To discuss the ligand T_2 process in uranium compounds, we start from the spin-spin terms in the nuclear spin Hamiltonian, which may be written as $H_{SS} = H_{AA} + H_{AB} + H_{BB}$, where

the A spins (I_i) are the ligand nuclear spins observed by NMR and the B spins (S_k) are the ^{235}U nuclei. H_{BB} is probably unimportant for the A -spin echo decay and therefore dropped, and H_{AA} and H_{AB} can be specified in general as

$$H_{AA} = \sum_{i>j} \alpha_{ij} I_{zi} I_{zj} + \sum_{i\neq j} \beta_{ij} I_{+i} I_{-j}, \quad H_{AB} = \sum_{ik} \gamma_{ik} I_{zi} S_{zk}. \quad (2)$$

In the A -spin echo decay process, the importance of the dynamical β_{ij} term depends on whether there is significant short-range inhomogeneous line broadening present. In URh_3 the A -spin (^{103}Rh) echo signal was observed to undergo Gaussian decay (figure 1(a)). Further, the decay rate constant $1/T_{2G}$ has been found to vary as $1/T_{2G}^2 \propto (1 - \cos \theta)$, where θ is the rotation angle of the refocusing pulse (not shown). This result indicates that the dynamical β_{ij} term is almost totally ineffective, i.e., the like-spin broadening is completely static. Therefore, the like-spin (T_{2G}) decay process only occurs because of spin re-orientation caused by the refocusing pulse in the spin-echo sequence.

For the γ_{ik} term, if the B spins (i.e., ^{235}U) were static on the timescale of the like-spin decay (≈ 13 ms in URh_3), this interaction would have no effect on the A -spin echo decay. In the other limit, when the narrowing parameter $\langle \Delta\omega^2 \rangle_{AB}^{1/2} T_{1B} \ll 1$, the cross-relaxation process becomes strongly narrowed. The decay function can then be written as

$$m_{2A}(\tau) = f_{2A}(\tau) \exp(-\langle \Delta\omega^2 \rangle_{AB} T_{1B} \tau), \quad (3)$$

where $f_{2A}(\tau)$ is the decay function in the absence of the B spins [4]. The formula given is quite general and, for example, can be derived with the standard motional narrowing formula for T_2 [6], $T_2^{-1} = \langle \Delta\omega^2 \rangle \int_0^\infty g(\tau) d\tau$, where $g(\tau)$ is the autocorrelation function for the interaction which generates the second moment $\langle \Delta\omega^2 \rangle$. In our case, we have simply $g(\tau) = e^{-\tau/T_{1B}}$ [4]. Such an additional Lorentzian decay process is indeed observed in the enriched sample as $\exp(-\tau/T_{2L})$ (equation (1)).

We next consider the temperature dependence of $m_{2A}(\tau)$ in the case of B spins which have a Korringa-like T_{1B} process. At very high (low) temperatures, T_{1B} will be extremely short (long) compared with the timescale of T_{2AA} ($\equiv T_{2G}$, equation (1)), and thus the decay will be governed by the like-spin coupling alone. In between, T_{1B} will cross the timescale of T_{2G} , and if $\langle \Delta\omega^2 \rangle_{AB}$ is comparable to $\langle \Delta\omega^2 \rangle_{AA}$ there will be a peak in the spin-echo decay rate at or near the point where $\langle \Delta\omega^2 \rangle_{AB} T_{1B}^2 \approx 1$. The value of $1/T_{2L}$ at the peak temperature roughly corresponds to the square root of the unlike-spin second moment³, i.e., $1/T_{2L}^{peak} \approx \langle \Delta\omega^2 \rangle_{AB}^{1/2}$. In URh_3 the 5f electrons are itinerant, suggesting that T_{1B} (i.e., $^{235}\text{T}_1$) would show a Korringa-like T dependence, as does the ^{103}Rh . The observed cross-relaxation effect is consistent with this premise. Correspondingly, from $1/T_{2L}^{peak} \approx 80 \text{ s}^{-1}$ we then obtain $\langle \Delta\omega^2 \rangle_{AB} \approx 6.4 \times 10^3 \text{ s}^{-2}$. This yields, finally, $^{235}\text{T}_1 T \approx 2 \text{ s K}$.

4. Summary

We have observed the cross-relaxation effect of T_1 -modulated ^{235}U spins on the spin-echo decay of ligand ^{103}Rh nuclei in URh_3 and have estimated the T_1 of ^{235}U to vary as $^{235}\text{T}_1 T \approx 2 \text{ s K}$. This is, to our knowledge, the first measurement of $^{235}\text{T}_1$ reported for a metallic uranium compound. The estimated temperature dependence $^{235}\text{T}_1 T \sim 2 \text{ s K}$ indicates that $^{235}\text{T}_1 \sim 500 \text{ ms}$ at 4.2 K. Thus, it would be possible, in principle, to detect the ^{235}U NMR signal directly using the standard pulsed NMR technique in this system. Finally, we note that the like-spin and unlike-spin second moments obtained, $\langle \Delta\omega^2 \rangle_{AA}$ and $\langle \Delta\omega^2 \rangle_{AB}$, both exceed the values expected from dipolar interactions alone: $\langle \Delta\omega^2 \rangle_{AA}^{dipolar} \approx 6.26 \times 10^3 \text{ s}^{-2}$,

³ At the peak of $1/T_{2AB}$, $\langle \Delta\omega^2 \rangle_{AB} T_{1B}^2 \approx 1$. Thus, from equation (3), $1/T_{2AB}^{peak} = \langle \Delta\omega^2 \rangle_{AB} T_{1B}^{peak} \approx \langle \Delta\omega^2 \rangle_{AB}^{1/2}$.

and⁴ $\langle \Delta\omega^2 \rangle_{AB}^{\text{dipolar}} \approx 1.18 \times 10^3 \text{ s}^{-2}$. This indicates that there is significant indirect (RKKY) spin–spin coupling in this system. The T_2 method employed here for URh_3 should be widely applicable for estimation of $^{235}\text{T}_1(T)$ in other uranium compounds.

Acknowledgments

We would like to acknowledge the useful collaboration of S Takagi, who first estimated T_1 of ^{235}U to be $^{235}\text{T}_1 T \sim 1 \text{ s K}$ using the electronic specific heat coefficient $\gamma_{el} \sim 14 \text{ mJ K}^{-2} \text{ mol}^{-1}$ reported for URh_3 [7]. His estimates stimulated us to make measurements of $^{235}\text{T}_1$ in metallic uranium compounds.

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⁴ Here we have used the first two neighbour shells of the URh_3 lattice and the lattice constant $a = 4.0 \text{ \AA}$ to estimate $\langle \Delta\omega^2 \rangle_{AA}^{\text{dipolar}}$. For $\langle \Delta\omega^2 \rangle_{AB}^{\text{dipolar}}$, we have used only the nearest-neighbour shell with 20% ^{235}U enrichment.