NMR and NQR studies of URu$_2$Si$_2$ and isostructural nonmagnetic references

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Abstract. The non-$f$ compound ThRu$_2$Si$_2$ has been studied as an isostructural nonmagnetic reference for URu$_2$Si$_2$ using nuclear magnetic resonance (NMR) measurement. The temperature dependences of Knight shifts measured by $^{29}$Si-NMR and $^{99}$Ru-NMR are independent of temperature. The results are consistent with data previously reported on the susceptibility. $^{101}$Ru-NQR frequency $^{101}v_Q$ was also estimated from the $^{99}$Ru-NMR measurement. $^{101}v_Q$ of ThRu$_2$Si$_2$ is close to that of URu$_2$Si$_2$, especially at high temperatures, suggesting that U ions in URu$_2$Si$_2$ are in a nearly tetravalent state.

1. Introduction
The uranium heavy fermion URu$_2$Si$_2$ undergoes a mysterious phase transition, so-called “Hidden order (HO)”, at $T_{HO} = 17.5$ K and an unconventional superconducting transition at $T_c = 1.4$ K [1, 2, 3]. Although intensive studies have been made on this compound, the mechanisms of these intriguing phenomena are still unclear.

To obtain detailed information on electronic states controlling physical properties in URu$_2$Si$_2$, it is very useful to compare this compound with nonmagnetic references experimentally. In our previous paper [4], we reported the results of nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) measurements on two isostructural non-$f$ compounds ThRu$_2$Si$_2$ and LaRu$_2$Si$_2$, and the comparison of the obtained results with already known data on URu$_2$Si$_2$ [5, 6] allowed us to extract new information on U valence and spin-fluctuation character of URu$_2$Si$_2$ [4]. However, it seems that the reference compounds, especially ThRu$_2$Si$_2$, have not been fully experimentally investigated so far. Therefore we show the first Knight shift data, to our knowledge, on ThRu$_2$Si$_2$ in this paper.

2. Experimental details
High quality single crystals of ThRu$_2$Si$_2$ were grown in a tetra-arc furnace under high-purity Ar gas atmosphere by the Czochralski method. The details of the sample preparation are described
elsewhere [7]. The single crystalline sample was used for the measurement of $^{99}$Ru-NMR. We also used a collection of many small single crystals for $^{101}$Ru-NQR and $^{29}$Si-NMR measurements. All the NMR and NQR experiments were carried out by a spin-echo technique with a phase-coherent pulsed spectrometer.

3. Results and Discussion

![Figure 1](image.png)

Figure 1. Temperature dependences of $^{29}K_{\|}$ and $^{29}K_{\perp}$ of ThRu$_2$Si$_2$ measured by $^{29}$Si-NMR at a field of 6.0 T. The broken lines are guides to the eye.

Figure 1 shows the temperature dependences of the Knight shifts measured by $^{29}$Si-NMR in ThRu$_2$Si$_2$. $^{29}K_{\|}$ and $^{29}K_{\perp}$ indicate Knight shift components for magnetic fields parallel and perpendicular to the crystal $c$ axis, respectively. The Knight shift is generally in a linear relationship with the susceptibility $\chi$. Therefore the facts that these Knight shifts, especially $^{29}K_{\|}$, show much smaller value than those for URu$_2$Si$_2$ and that they are almost independent of temperature are in good agreement with the temperature dependence of $\chi$ [8]. The anisotropic part of the shift, $^{29}K_{\text{aniso}} = \left( ^{29}K_{\|} - ^{29}K_{\perp} \right) / 3$, is $\sim 1 \times 10^{-2} \%$, which is almost consistent with our previous report [4]. The data in Fig. 1 are somewhat scattered, which is owing to slightly ambiguous line shapes. Since our sample was not a fine powder, the observed line shape could slightly deviate from an ideal powder pattern.

Next we show the results of NMR measurements at the Ru site. Our single crystal has a cone shape (see the upper panel of Fig. 2). The sample was mounted in a coil and aligned by eye so that the $c$ axis is nearly perpendicular to field $B_0$. Since nuclear spin $I = 5/2$ for $^{99}$Ru, we observed a central line corresponding to the $1/2 \leftrightarrow 1/2$ transition and nuclear quadrupole-split lines. In Fig. 2, the right panel shows the central line and the left panel shows the first satellite line corresponding to the $1/2 \leftrightarrow 3/2$ transition. To extract information on the Knight shift from the data, we used the following nuclear spin Hamiltonian;

$$\mathcal{H} = \gamma h B_0 \cdot \left( \mathbf{I} + \mathbf{K} \right) \cdot \mathbf{I} + \mathcal{H}_Q,$$

(1)

where $\gamma$ is the gyromagnetic ratio, $\mathbf{K}$ is the Knight shift tensor, and $\mathcal{H}_Q$ is the Hamiltonian describing nuclear quadrupole interaction. The crystal structure of ThRu$_2$Si$_2$ possesses a fourfold symmetry around the $c$ axis, and $\mathcal{H}_Q$ is given by

$$\mathcal{H}_Q = (h\nu_Q/6) \left( 3I_z^2 - I^2 \right),$$

(2)
where $z \parallel c$. Since NQR frequency $^{99}\nu_Q$ at 4.2 K is estimated to be 1.046 MHz from the observation of $^{101}\text{Ru-NQR}$ signal in zero field [4, 9], we can fit the spectra at 4.2 K to Eq. (1) with two fit parameters: an angle $\theta$ between the $c$ axis and $B_0$ and the Knight shift $K(\theta)$ along $B_0$. The fit gives $\theta = 85 \pm 0.5$ degrees. Since $\theta$ should be fixed throughout the measurement, the spectra from 20 to 83 K can be fit with two fit parameters $K(\theta, T)$ and $^{99}\nu_Q(T)$. The results are shown in Fig. 3(a). The value of $^{99}K_\perp$ in Fig. 3(a) was obtained by correcting $^{99}K_\parallel$ using $^{99}K_{\text{aniso}} = -0.05\%$ and a relation of $K(\theta) = K_\parallel \cos^2 \theta + K_\perp \sin^2 \theta$. Here, $^{99}K_{\text{aniso}}$ was estimated by fitting a powder pattern spectrum measured at 4.2 K (not shown), and we neglected the temperature dependence of $^{99}K_\parallel$ above 20 K.

The Knight shifts for both Si and Ru sites are anisotropic, $^{29}\left(K_\perp/K_\parallel\right) \sim 0.61$ and $^{99}\left(K_\perp/K_\parallel\right) \sim 1.3$, respectively, however their anisotropy are not as large as in $\chi$ ($\chi_\perp = 8.5 \times 10^{-5}$ and $\chi_\parallel < 10^{-11}$ emu/mol [8]). Generally, $\chi$ in nonmagnetic metals is a sum of diamagnetic, Van Vleck, and Pauli paramagnetic (p.p.) susceptibilities. Note that spin lattice relaxation rate $1/T_1$ at the Si site shows an isotropic Korringa relation [4], i.e. $^{29}\left(1/T_1 T\right)_\parallel = ^{29}\left(1/T_1 T\right)_\perp$, indicating predominant isotropic coupling between Si nuclei and conduction electrons. This also suggests that considerable isotropic part of $^{29}K$ arises from the p.p.-susceptibility. Therefore one naively expects the existence of non-negligible diamagnetic component as well as the isotropic p.p.-susceptibility to reproduce the extremely small $\parallel$ [8].

The analysis of the data in Fig. 2 also gives the estimation of $^{101}\nu_Q$ at the Ru site. We plot in Fig. 3(b) the temperature dependence of $^{101}\nu_Q$ for ThRu$_2$Si$_2$ together with that of URu$_2$Si$_2$ [10]. The weak temperature dependence for ThRu$_2$Si$_2$ is in contrast to the data on URu$_2$Si$_2$. The anomalous temperature dependence for URu$_2$Si$_2$ is ascribed to temperature-induced changes in electronic configuration which is accompanied by a change in the U valence. Note that $^{101}\nu_Q$’s

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Figure 2. Upper panel: Single crystalline sample of ThRu$_2$Si$_2$ used for the present experiments. Lower left and right panels show the first satellite line and the central line of $^{99}\text{Ru-NMR}$, respectively. The spectra were measured by applying magnetic fields of $\sim 13.5$ T nearly perpendicular to the $c$ axis.
of the two compounds are close to each other, especially at high temperatures. Generally $\nu_Q$ is influenced by changes in local charge distribution around the nucleus. For lanthanide based compounds, there are several examples showing that $\nu_Q$ at ligand sites significantly varies reflecting the valence change of lanthanide ions (for example see Ref. [4]). Therefore, the result may suggest that the valence of U ions at high temperature is close to Th valence, namely 4+. Interestingly, $^{101}\nu_Q$ at the Ru site in LaRu$_2$Si$_2$, in which La ions are supposed to be trivalent, is roughly twice larger than those for URu$_2$Si$_2$ and ThRu$_2$Si$_2$ [4]. A theoretical calculation attempting the reproduction of these $\nu_Q$’s will be crucial for microscopic understanding of electronic states in these compounds.

4. Summary
We have carried out $^{29}$Si- and $^{99}$Ru-NMR measurements on the non-$f$ compound ThRu$_2$Si$_2$ as a nonmagnetic reference for URu$_2$Si$_2$. The results are the first detailed NMR data on ThRu$_2$Si$_2$ to our knowledge. Both Knight shifts measured by $^{29}$Si- and $^{99}$Ru-NMR are independent of temperature, in good agreement with the temperature dependence of $\chi$. The temperature dependence of $\nu_Q$ at the Ru site is much weaker than the data on URu$_2$Si$_2$, suggesting electronic configuration in URu$_2$Si$_2$, including 5$f$ electrons, considerably changes with temperature. From the close values of $\nu_Q$ in ThRu$_2$Si$_2$ and URu$_2$Si$_2$, it is likely that the U ions in URu$_2$Si$_2$ are in a nearly tetravalent state rather than in a trivalent state especially at high temperatures.

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