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Magnetic and Electronic Properties of URu_2Si_2 Revealed by Comparison with Nonmagnetic References $ThRu_2Si_2$ and $LaRu_2Si_2$

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We have carried out nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) measurements on $ThRu_2Si_2$ and $LaRu_2Si_2$, which are the nonmagnetic references of the intriguing heavy fermion URu_2Si_2. The comparisons of URu_2Si_2 with the reference materials allow us to analyze the already known NMR and NQR data on URu_2Si_2 phenomenologically and semiquantitatively. The study of ^{101}Ru-NQR frequency suggests the relatively close electronic configuration of URu_2Si_2, including the valence of the actinide ion, to that of the tetravalent $ThRu_2Si_2$ at high temperatures, as well as the delocalization of 5f electrons at low temperatures. Ising-like spin fluctuations along the c-axis were brought to light by ^{29}Si-NMR data in the so-called hidden order phase of URu_2Si_2. The unique magnetic property is plausibly associated with the mechanism of the unconventional superconductivity.

The uranium heavy fermion URu_2Si_2 has been attracting much interest since its discovery almost 30 years ago[1–3] because of its fascinating properties, including the mysterious phase transition at $T_{HO} = 17.5$ K, whose order parameter has not been identified [so-called "hidden order (HO)"], and its unconventional superconductivity below $T_c = 1.4$ K. Among a wide variety of experimental reports on this compound, studies using nuclear magnetic resonance (NMR) have played an important role in providing microscopic information on the issues of the HO and superconducting phases: for example, a decrease in the density of states at Fermi energy[4,5] and spurious antiferromagnetic ordering[6] in the HO phase, and the existence of line nodes in superconducting energy gap.[4,5] Moreover, symmetry changes across the HO have recently been discussed from the magnetic[7–9] and electronic[10] points of view.

However, we have noticed that some pieces of fundamental information on magnetic fluctuations and U-valence have been missing owing to the lack of comparisons between the NMR data of URu_2Si_2 and its nonmagnetic references so far. In this paper, we report on the results of NMR and nuclear quadrupole resonance (NQR) measurements performed on the two isostructural non-f compounds $ThRu_2Si_2$ and $LaRu_2Si_2$. The comparisons of already reported NMR and NQR data on URu_2Si_2[4,5] with the present results allow us to analyze them semiqualitatively and to extract unique information on the magnetic and electronic properties of URu_2Si_2. First, we discuss whether $ThRu_2Si_2$ is suitable as the nonmagnetic reference of URu_2Si_2 on the basis of the NQR data measured at the Ru site. The NQR frequency ν_Q sensitively reflects local charge distribution. Then, by comparing the nuclear spin lattice relaxation rate $1/T_1$ data of URu_2Si_2 with those of $ThRu_2Si_2$, we conclude that there exist only spin fluctuations along the crystal c-axis in the HO phase and these Ising-like fluctuations may be important for the appearance of the unconventional superconductivity in URu_2Si_2.

The single crystals of $ThRu_2Si_2$ 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.[11] A single crystal sample was used for the estimation of the temperature dependence of ν_Q at the Ru site by ^{99}Ru-NMR measurement. Most of other the ^{29}Si-NMR (nuclear spin $^{29}I = 1/2$), ^{99,101}Ru-NMR ($^{99,101}I = 5/2$), and ^{101}Ru-NQR measurements on $ThRu_2Si_2$ were performed using a powdered sample. A polycrystalline sample of $LaRu_2Si_2$ was also synthesized by arc-melting constituent elements in Ar atmosphere, and we measured the ^{101}Ru-NQR spectra of this sample. All the NMR and NQR experiments were carried out by the spin-echo technique with a phase-coherent pulsed spectrometer. T_1 was measured by a single rf-pulse saturation method.

The U ion in URu_2Si_2 has been regarded to be between U^{3+} ($5f^3$) and U^{4+} ($5f^2$) configurations. Actually, many theoretical models to explain the various properties of URu_2Si_2 seem based on the regime starting from the $5f^2$ configuration.[12] However, it is difficult to distinguish experimentally these two valences. One of the reasons is that the two 5f electron states have quite close values of effective moment (3.62 and 3.58 μ_B for U^{3+} and U^{4+}, respectively), whose magnetic responses are indistinguishable. Therefore, we focused on the data on ν_Q, which is sensitive to local charge distribution.

Figure 1(a) shows a field-swept ^{99}Ru-NMR line of $ThRu_2Si_2$. The spectrum consists of two peaks around 12.0 T arising from a transition between the nuclear spin states of $-1/2 \leftrightarrow 1/2$ and the two quadrupole-split first satellite lines ($\pm 1/2 \leftrightarrow \pm 3/2$) of ^{99}Ru-NMR. An additional resonance peak indicated by an arrow is assigned to one of the two first satellites of ^{101}Ru-NMR. From the obtained spectrum, we were able to extract $^{99}\nu_Q = 1.046$ MHz for the ^{99}Ru nucleus, yielding $^{101}\nu_Q = 6.05$ MHz for the ^{101}Ru nucleus using the ratio of nuclear quadrupole moments, $^{101}Q/^{99}Q = 457/79$.[13] This estimation was verified by the

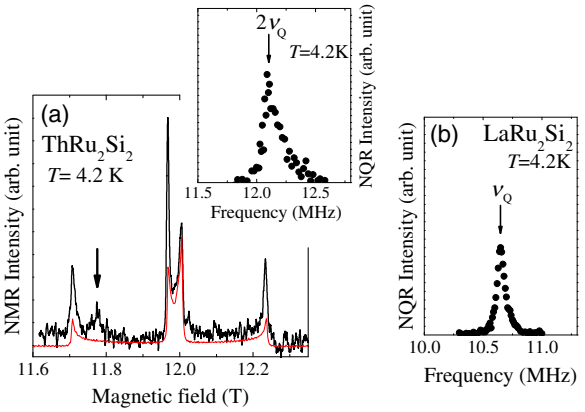

Fig. 1. (Color online) (a) Ru-NMR spectrum of $ThRu_2Si_2$ measured at 4.2 K and a frequency of 23.56 MHz. The solid line shows a calculated spectrum with $^{99}\nu_Q = 1.046$ MHz. The peak indicated by the arrow is assigned to one of the two first satellites of ^{101}Ru-NMR. Inset: ^{101}Ru-NQR spectrum measured at 4.2 K and a frequency corresponding to a $\pm 3/2 \leftrightarrow \pm 5/2$ transition, i.e., $2 \times {}^{101}\nu_Q$. (b) ^{101}Ru-NQR spectrum of $LaRu_2Si_2$ measured at 4.2 K and $^{101}\nu_Q$. The measurement of the ^{101}Ru-NQR spectrum was performed at $^{101}\nu_Q$ because the spectrum at $2 \times {}^{101}\nu_Q$ overlaps with the tail of the $3 \times {}^{139}\nu_Q$ line of ^{139}La-NQR with $I = 7/2$ and $^{139}\nu_Q = 7.01$ MHz.

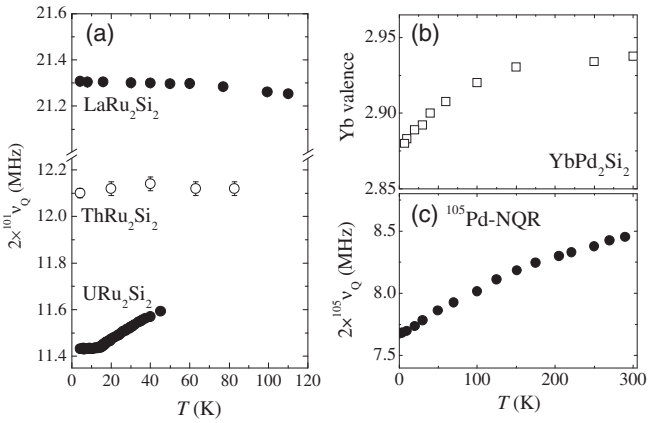

Fig. 2. (a) Temperature dependences of $2 \times {}^{101}\nu_Q$ for URu_2Si_2,[10] $LaRu_2Si_2$, and $ThRu_2Si_2$. The $ThRu_2Si_2$ data for $T \geq 20$ K were estimated from ^{99}Ru-NMR measurement of a single crystal owing to the poor signal intensity of ^{101}Ru-NQR. Other data were obtained from ^{101}Ru-NQR measurements. (b) Temperature dependence of the Yb valence of the valence-fluctuating compound $YbPd_2Si_2$ evaluated from X-ray absorption spectroscopy measurement.[17] (c) Temperature dependence of $2 \times {}^{105}\nu_Q$ obtained from the ^{105}Pd-NQR measurement.

observation of a ^{101}Ru-NQR signal at a frequency of 12.1 MHz $= 2 \times {}^{101}\nu_Q$, as shown in the inset of Fig. 1(a). At the Ru site with fourfold symmetry along the c-axis, the ratio of NQR frequencies $\nu_Q : \nu_Q(2) = 1 : 2$, where ν_Q and $\nu_Q(2)$ are resonance frequencies for the transitions between $\pm 1/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 5/2$, respectively.

Note that the $^{101}\nu_Q$ of URu_2Si_2 [$^{101}\nu_Q(URu_2Si_2) = 5.72$ MHz[5,10,14)]] is close to that of $ThRu_2Si_2$ [$^{101}\nu_Q(ThRu_2Si_2) = 6.05$ MHz] in which the Th ion is tetravalent. Actually, it is difficult to estimate ionic valence quantitatively only from the ν_Q data. However, if we see how ν_Q changes in valence transition or valence-fluctuating systems (see, for example, Ref. 15 and the case of $YbPd_2Si_2$ described below), the present small difference in $^{101}\nu_Q$ (~ 0.3 MHz) between URu_2Si_2 and $ThRu_2Si_2$ suggests the similarity of electronic configuration, except for 5f electrons, between the two compounds.

$^{101}\nu_Q(ThRu_2Si_2)$ shows weak temperature dependence, as shown in Fig. 2(a). A more precise temperature dependence of $^{101}\nu_Q$ was measured for $LaRu_2Si_2$ in order to obtain further information on electronic states in URu_2Si_2. $^{101}\nu_Q(LaRu_2Si_2)$ estimated as 10.65 MHz at 4.2 K [see Fig. 1(b)] is close to $^{101}\nu_Q = 10.52$ MHz for $CeRu_2Si_2$,[16)] both of which are trivalent or quasitrivalent compounds. On the other hand, $^{101}\nu_Q(LaRu_2Si_2)$ is $\sim$1.9 times larger than $^{101}\nu_Q(ThRu_2Si_2)$. The difference is predominantly attributed to the difference in the charge distribution between the two systems. This result also supports the fact that the U valence is closer to 4+ rather than 3+, so that we found that $ThRu_2Si_2$ is applicable as the nonmagnetic reference of URu_2Si_2.

One should also notice that the temperature dependence of $^{101}\nu_Q(URu_2Si_2)$ contrasts with that of $^{101}\nu_Q(LaRu_2Si_2)$. $^{101}\nu_Q(LaRu_2Si_2)$ shows a gradual decrease with increasing temperature, as seen in the upper panel of Fig. 2(a), which is a characteristic behavior reflecting a normal thermal expansion of the lattice. The result suggests that no significant rearrangement of charge distribution occurs with temperature, namely, the La ion is in a stable trivalent state. In this context, we may expect a somewhat similar temperature dependence for $^{101}\nu_Q(ThRu_2Si_2)$ as well.

On the other hand, $^{101}\nu_Q(URu_2Si_2)$ increases with temperature above T_{HO}. Therefore, the difference between $^{101}\nu_Q(URu_2Si_2)$ and $^{101}\nu_Q(ThRu_2Si_2)$ ($\sim$0.3 MHz at 4.2 K as mentioned above) is even smaller at higher temperatures, suggesting a closer electronic configuration between these two compounds at high temperatures. The decrease in ν_Q in the low-temperature region is generally observed in valence-fluctuating lanthanide compounds, where the positive valence of lanthanide ions simultaneously decreases upon cooling. We found that the temperature dependence of $^{101}\nu_Q(URu_2Si_2)$ is analogous to that of the isostructural Yb compound $YbPd_2Si_2$. Here, the Yb valence was studied by X-ray absorption spectroscopy,[17)] as shown in Fig. 2(b). As temperature decreases, the delocalization of 4f electrons is induced owing to the evolution of exchange interactions between conduction and 4f electrons, resulting in the decrease in the Yb valence (valence-fluctuating state) and simultaneously in $\nu_Q(YbPd_2Si_2)$ [see Fig. 2(c)]. Similarly, the temperature dependence of $^{101}\nu_Q(URu_2Si_2)$ revealed in Fig. 2(a) suggests the delocalization of U-5f electrons at low temperatures. For a more quantitative discussion, reliable theoretical calculations are required.

Next, we show the results of ^{29}Si-NMR measurements. The ^{29}Si-NMR line exhibits a slightly asymmetric powder pattern, as seen in Fig. 3, implying that it consists of small anisotropic components of the Knight shift K. However, the evaluated anisotropic component of the shift is quite small: $K_{aniso} = 8 \times 10^{-3}$%. Therefore, compared with the strongly anisotropic Knight shift of URu_2Si_2,[4)] the shift is regarded to be almost isotropic. As discussed in Ref. 4, the hyperfine coupling constant of URu_2Si_2 is isotropic, and the present results are consistent with this.

By measuring the intensities of the ^{29}Si-NMR signal near the frequencies indicated by arrows in Fig. 3, we could estimate $1/T_1$ of $ThRu_2Si_2$ [hereafter denoted as $^{Th}(1/T_1)$]

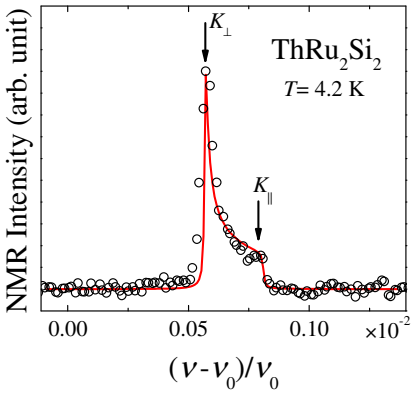

Fig. 3. (Color online) Fourier-transformed spectrum of ^{29}Si-NMR measured at 4.2 K and an external field of $H_0 = 5.9998$ T. The horizontal axis indicates the evaluated shift, where $\nu_0 = {}^{29}\gamma_n/2\pi \times H_0$ with ${}^{29}\gamma_n/2\pi = 8.4577$ MHz/T. The signal intensity near the frequency regions indicated by arrows was used to estimate T_1 components for $H \parallel c$ and $H \perp c$.

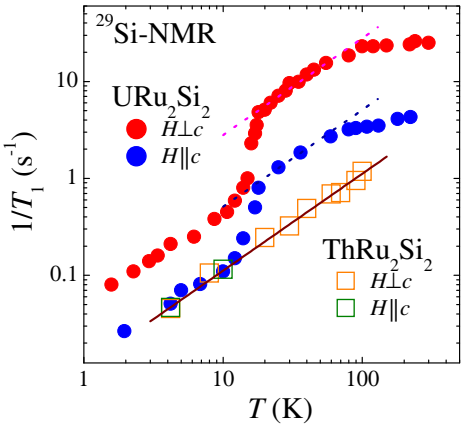

Fig. 4. (Color online) Temperature dependence of $1/T_1$ measured by ^{29}Si-NMR. The previous data of URu_2Si_2[4] are compared with the present results for $ThRu_2Si_2$. The solid line is a linear fit to the data for $H \perp c$, and the broken lines indicate Korringa-like behavior for URu_2Si_2 above T_{HO}.

for $H \parallel c$ and $H \perp c$, i.e., ${}^{Th}(1/T_1)_\parallel$ and ${}^{Th}(1/T_1)_\perp$, respectively. Their temperature dependences are shown in Fig. 4, along with the previously reported data on URu_2Si_2 [${}^{U}(1/T_1)$].[4] ${}^{Th}(1/T_1)_\perp$ shows the so-called Korringa relation

$$ {}^{Th}(1/T_1)_\perp = 0.0112T, \tag{1}$$

which is a characteristic behavior of a Fermi liquid. Although we were able to measure ${}^{Th}(1/T_1)_\parallel$ only up to 10 K owing to a poor signal-to-noise ratio, the result indicates that ${}^{Th}(1/T_1)$ is isotropic within experimental accuracy. For $T > T_{HO}$, we assume that Eq. (1) corresponds to a contribution from conduction electrons without $5f$ electrons in URu_2Si_2. As indicated in Ref. 4, ${}^{U}(1/T_1)$ shows the Korringa relation above T_{HO}, as shown by dotted lines in Fig. 4. Since $1/T_1T$ is generally proportional to $D(\varepsilon_F)^2$, with $D(\varepsilon_F)$ being the density of states at Fermi energy, the enhancement of ${}^{U}(1/T_1)$ compared with ${}^{Th}(1/T_1)$ above T_{HO} implies the formation of a heavy Fermi liquid owing to the Kondo effect.

A remarkable feature shown in Fig. 4 is that ${}^{U}(1/T_1)_\parallel$ abruptly decreases to the line expressed by Eq. (1) below T_{HO}. $(1/T_1)_\parallel$ and $(1/T_1)_\perp$ are related to the dynamical susceptibilities perpendicular and parallel to the c-axis, $\chi_\perp(q,\omega_0)$ and $\chi_\parallel(q,\omega_0)$, respectively, as follows:

$$\left(\frac{1}{T_1}\right)_\parallel = \frac{2\gamma_n^2 k_B T}{(\gamma_e\hbar)^2}\sum_q\left[A_{hf,\perp}^2\frac{\mathrm{Im}\chi_\perp(q,\omega_0)}{\omega_0}\right], \tag{2}$$

and

$$\left(\frac{1}{T_1}\right)_\perp = \frac{\gamma_n^2 k_B T}{(\gamma_e\hbar)^2}\sum_q\left[A_{hf,\parallel}^2\frac{\mathrm{Im}\chi_\parallel(q,\omega_0)}{\omega_0} + A_{hf,\perp}^2\frac{\mathrm{Im}\chi_\perp(q,\omega_0)}{\omega_0}\right], \tag{3}$$

where γ_n and γ_e are the nuclear and electronic gyromagnetic ratios, respectively, ω_0 is the NMR frequency, $\mathrm{Im}\chi_i(q,\omega_0)$ is the imaginary part of $\chi_i(q,\omega_0)$ ($i = \parallel$ and $\perp$), and $A_{hf,\parallel} \approx A_{hf,\perp}$ for URu_2Si_2 and $ThRu_2Si_2$, as mentioned above. From Eq. (2), the decrease in ${}^{U}(1/T_1)_\parallel$ below T_{HO} implies that $\chi_\perp(q,\omega_0)$ in the HO phase is as small as that in the nonmagnetic metal $ThRu_2Si_2$.

On the other hand, $(1/T_1)_\perp$ predominantly obtains contribution from $\chi_\parallel(q,\omega_0)$, because $\chi_\perp(q,\omega_0)$ is small in Eq. (3). The anisotropy in ${}^{U}(1/T_1)$, which is in contrast to the case of $ThRu_2Si_2$, indicates the existence of magnetic correlations between electrons even in the Fermi liquid state. Therefore, the enhancement of ${}^{U}(1/T_1)_\perp$ in the HO phase is ascribed to the spin fluctuations existing only along the c-axis. Such a unique observation in URu_2Si_2 should be associated with the Ising-like magnetic property, which is revealed for example in the strongly anisotropic susceptibility: the magnetic signal along the a-axis is almost temperature-independent and several times smaller than that along the easy axis (c-axis).[1]

We briefly comment on the appearance of the superconductivity in URu_2Si_2. The superconductivity occurs in the lower-temperature region included by the HO phase having the Ising-type magnetic fluctuations, as mentioned above. If Cooper pairing is magnetically mediated there, the spin fluctuations along the c-axis should be responsible for the superconductivity, because the perpendicular component as small as those in $ThRu_2Si_2$ is unlikely to be the main driving force for the occurrence of the unconventional, anisotropic superconductivity. This regime is also consistent with the strong anisotropy in the upper critical field H_{c2}[18] [i.e., H_{c2} ($H \perp c$) > H_{c2} ($H \parallel c$)]: spin fluctuations will be considerably suppressed when applying magnetic field along the c-axis, leading to the depression of the superconductivity. Interestingly, a similar Ising anisotropy characterizes the magnetic properties in the U-based ferromagnetic (FM) superconductors URhGe and UCoGe,[19,20] in which FM fluctuations are intimately related to the appearance of superconductivity.[21]

Further information on the spin fluctuations detected by the present T_1 measurements is obtained using the modified Korringa relation for weakly correlated metals: $T_1TK_s^2 = SK(\alpha)^{-1}$, where K_s is the spin part of K, $S = \hbar/4\pi k_B(\gamma_e/\gamma_n)^2$, $K(\alpha) = (1-\alpha)^2[1-\alpha(\chi_0(q)/\chi_0(0))]^{-2}$, $(1-\alpha)^{-1}$ is an enhancement factor, and $\chi_0(q)$ is the dynamical susceptibility for noninteracting fermions.[22] At low temperatures in the HO phase, $K_{s,\parallel} = 0.31\%$,[23] being independent of temperature. Note that $K_{s,\parallel} \propto \chi_\parallel(0,0)$, and $\chi_\parallel(q,\omega_0)$ is probed by ${}^{U}(1/T_1)_{f,\perp} - {}^{U}(1/T_1)_{f,\parallel}/2$ from Eqs. (2) and (3), where ${}^{U}(1/T_1)_{f,i}$ ($i = \perp$ and $\parallel$) denotes $5f$ electronic components. Although ${}^{U}(1/T_1)_{f,i}$ may be extracted by subtracting the contribution of conduction electrons, it is indeed difficult to

estimate it correctly in the HO phase, because one needs to consider the reduction in carrier density below T_{HO}. Here, if we assume ${}^{U}(1/T_1)_{f,i} \sim {}^{U}(1/T_1)_i - {}^{Th}(1/T_1)_i$, which should give a lower limit of ${}^{U}(1/T_1)_{f,i}$, we obtain $K(\alpha) \ll 1$ for $H \parallel c$. This result does not vary even if we assume ${}^{U}(1/T_1)_{f,i} \sim {}^{U}(1/T_1)_i$, which should give an upper limit.

According to the modified Korringa relation, the result indicates FM correlations in the HO phase. On the other hand, one expects antiferromagnetic (AFM) correlations originating from the neighboring AFM order phase under pressure. Indeed, a magnetic excitation with the AFM wave vector $Q_0 = (1, 0, 0)$ was detected by an inelastic neutron measurement.[24] Here, to understand the present NMR result, we need to take into account the crystallographical surroundings of the Si site: it is located near an *ab* basal plane with four nearest-neighbor U ions. As expected from the Q_0 vector, the U magnetic moments tend to align ferromagnetically within the *ab* basal plane, so that they give rise to FM fluctuations that cannot be canceled out at the Si site. Thus, the T_1 relaxation is predominantly affected by the FM correlations owing to the geometrical factor; thus, the present result is not in disagreement with the AFM correlations between the planes.

In summary, the comparisons of already reported NMR and NQR data on URu_2Si_2 with the data on isostructural nonmagnetic references ($ThRu_2Si_2$ and $LaRu_2Si_2$) and a valence-fluctuating compound ($YbPd_2Si_2$) have uncovered some electronic and magnetic properties of URu_2Si_2. The data on ${}^{101}\nu_Q$ and its temperature dependence suggest that the U electronic configuration is close to $5f^2$ at high temperatures, while the $5f$ electrons gradually delocalize with decreasing temperature. From the $1/T_1$ data of ^{29}Si-NMR, we found Ising-like spin fluctuations along the *c*-axis in the HO phase. The unique magnetic property is plausibly associated with the mechanism of unconventional superconductivity.

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