NMR and NQR investigations of local symmetry in the hidden order phase of URu$_2$Si$_2$

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Abstract. In order to study local symmetries at the 4$e$-(Si)- and 4$d$-(Ru)-sites above and below hidden order transition temperature $T_O = 17.5$ K in URu$_2$Si$_2$, we have investigated the nuclear quadrupole interaction by $^{73}$Ge-nuclear magnetic resonance (NMR) measurement on a 10% $^{73}$Ge-substituted sample URu$_2$(Si$_{0.9}$Ge$_{0.1}$)$_2$, and by $^{101}$Ru-nuclear quadrupole resonance (NQR) measurement on a pure single crystal sample. The present $^{73}$Ge-NMR measurements do not give any evidence for change in the local symmetry at 4$e$-site within experimental accuracy. On the other hand, the precise measurement of $^{101}$Ru-NQR frequency has detected an anomaly just below $T_O$ as sensitively as the thermal expansion measurement does. Its temperature dependence shows a linear relation with that of the in-plane lattice parameter, which may be a clue to clarify a modification in microscopic charge distribution at $T_O$.

1. Introduction
The mysterious order at $T_O = 17.5$ K in URu$_2$Si$_2$, so called the “hidden order”, has been a topic of interest and controversy for more than two decades. In order to identify how symmetry of the system changes at $T_O$, information about local symmetry at each site has recently attracted considerable attention. In this context, investigation of the nuclear quadrupole interaction, which can be probed by nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) measurements, is useful, because it detects the modification of local charge distribution as follows: the nuclear spin $I$ (restricted to $I \geq 1$) interacts with the electric-field gradient (EFG) caused by surrounding charges through $\mathcal{H}_Q = (\hbar \nu_Q/6) \left[ 3I_z^2 - I^2 + \eta \left( I_x^2 - I_y^2 \right) \right]$, where $\nu_Q$ is the NQR frequency of the $\pm 1/2 \leftrightarrow \pm 3/2$ transition, $Q$ is the quadrupolar moment of the nucleus, the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, and $V_{\alpha\alpha}$ is EFG at the nuclear position along the $\alpha$ direction, following $V_{zz} \geq V_{xx} \geq V_{yy}$. In this paper, we report the results of the measurements of the nuclear quadrupole interactions at the 4$e$-(Si)- and 4$d$-(Ru)-sites. For the 4$e$-site, because $^{29}$Si nuclear spin ($I = 1/2$) does not couple to the EFG, we performed $^{73}$Ge-NMR measurement on a partially $^{73}$Ge-substituted sample, URu$_2$(Si$_{1-x}$Ge$_x$)$_2$. 

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2. Experimental details

We prepared two kinds of samples; a single crystalline sample of URu$_2$Si$_2$ and a 10% Ge-substituted polycrystalline sample, URu$_2$(Si$_{0.9}$Ge$_{0.1}$)$_2$. The latter was prepared by arc-melting constituent elements together in an argon atmosphere. Enriched $^{73}$Ge (98%) with minimum purity of 99.9% was used for the substitution, which enables us to measure the nuclear quadrupole interaction at the 4e-site due to $^{73}I = 9/2$. With this sample, we have also measured the susceptibility $\chi$ by a commercial SQUID magnetometer at a field $B = 1$ T, and the specific heat $C$ using the adiabatic heat pulse method. As for the single crystal, which was grown along the tetragonal $a$ axis by the Czochralski technique in a tri-arc furnace, we have measured $^{101}$Ru-NQR as well as the thermal expansion. The thermal expansion was measured using the strain gauge technique with a copper block as a dummy sample. All the NMR and NQR experiments were carried out by using the spin-echo technique with a phase-coherent pulsed spectrometer.

3. Results and Discussion

Figure 1 shows the $T$-dependences of $\chi$ and $C/T$ for the URu$_2$(Si$_{0.9}$Ge$_{0.1}$)$_2$ sample. A second-order transition is clearly observed, which indicates that the transition is still a bulk property. This is consistent with a previous report [1]. Both maxima of $C/T$ and $d\chi/dT$ give $T_O \sim 16.5$ K. Because $T_O$ increases with pressure [2], the slightly lower transition temperature than in pure URu$_2$Si$_2$ is explained in terms of a negative pressure effect due to the partial substitution of Si with larger Ge.

![Figure 1](image1.png)

**Figure 1.** $T$-dependences of $\chi$ (solid circles) and $C/T$ (open circles) [3] for the 10% Ge-substituted sample URu$_2$(Si$_{0.9}$Ge$_{0.1}$)$_2$. Inset shows $T$-derivative of $\chi$, $d\chi/dT$, as a function of $T$.

Figure 2 shows $^{73}$Ge-NMR lines for $B \perp c$ measured above and below $T_O$. Note we used an oriented powder sample along the $c$-axis by using strongly anisotropic magnetization. This alignment method leaves a random distribution of $a$-$b$ basal-plane orientations. Although the data are somewhat scattered because of very weak signal intensity, we observed the definite effect of the nuclear quadrupole interaction which is characterized by $\nu_Q = 0.43$ MHz [3]. If the local symmetry at the 4e-site is lowered below $T_O$, one expect a change in lineshape in the order state. For example, a breakdown of 4-fold symmetry should give rise to a non-zero $\eta$ value at this site, resulting in a line broadening and/or splitting of quadrupole-split satellite peaks. As
a result of more intensive measurements than in our previous report [3], no systematic change in the lineshape was observed. The present experimental accuracy yields $\eta < 0.1$ at the 4e-site below $T_O$ [3], which may not be enough accurate to conclude the absence of the breakdown of the 4-fold symmetry in the hidden order phase. We therefore need more precise measurements for this issue.

Figure 3 shows the $T$-dependence of $^{101}$Ru-NQR line measured near the frequency of the $\pm 3/2 \leftrightarrow \pm 5/2$ transition, $\nu_Q(2)$. While the spectrum is almost independent of $T$ below $T_O$, it gradually shifts to higher frequency with $T$ above $T_O$. No significant broadening was observed in the whole $T$-range of the experiment, consistent with previous reports [4, 5, 6]. $\nu_Q(2)$ obtained by a Lorentzian fit to the spectrum data is plotted as a function of $T$ in Fig. 4. The previous works [5, 6] observed no anomaly in $\nu_Q(T)$ around $T_O$. Our careful measurement however indicates a small deviation downward just below $T_O$ from a roughly linear $T$-dependence observed above $T_O$. This is also manifested by a maximum in the plot of $d\nu_Q(2)/dT$ vs $T$ just below $T_O$, as shown in the inset of Fig. 4. Structural anomaly at $T_O$ in URu$_2$Si$_2$ has been so far detected only by few experiments, including the thermal expansion measurement. The present result demonstrates that the NQR experiment probes the anomaly associated with the onset of the hidden order as sensitively as the thermal expansion measurement dose, as described later.

It is interesting to compare the $T$-dependence of $\nu_Q(2)$ with those of lattice parameters, since generally $\nu_Q(T)$ is supposed to be a function of a unit cell volume change $\Delta V(T)/V$. In Fig. 5(a) and (b), we show the $T$-dependences of the relative length changes along the $a$ and $c$ axes, $\Delta l_a/l_a$ and $\Delta l_c/l_c$, respectively. The result indicates that $\nu_Q(2)(T)$ cannot be expressed as a function of $\Delta l_c/l_c$, nor consequently $\Delta V(T)/V$, because $\Delta l_c/l_c$ shows a minimum around 33 K while $\nu_Q(2)(T)$ monotonically changes around this temperature. Instead, we have found that the $T$-dependence of $\nu_Q(2)$ is very similar to that of $\Delta l_a/l_a$. Actually the plot of the relative frequency change $\Delta \nu_Q(2)(T)/\nu_Q(2)$ vs $\Delta l_a(T)/l_a$ with $T$ as an implicit variable demonstrates a linear relation between them for $4 < T < 45$ K (see Fig. 6). The previous paper [5] indicated that $\nu_Q(2)(T)$ is not described by the $\Delta V(T)$ term, but by the singlet ground-state models for
the \( (5f)^2 \) configuration of \( U \) for \( T > T_0 \). On the other hand, our result reveals that the \( T \)-dependence of \( V_{zz} \) at the \( 4d \) site simply follows \( l_a(T) \) in the whole \( T \)-range of the measurement. This may be a clue to identify \( T \)-induced modification in the microscopic charge distribution.

4. Conclusion
We have investigated local symmetries at the \( 4d \)- and \( 4e \)-sites above and below the hidden order temperature in \( \text{URu}_2\text{Si}_2 \). The \( ^{73}\text{Ge-NMR measurement on a URu}_2(\text{Si}_{0.9}\text{Ge}_{0.1})_2 \) sample has not given any evidence for change in lineshape, namely in local symmetry at the \( 4e \)-site. We however may need to improve the experimental accuracy to obtain a conclusive evidence for this issue. On the other hand, the \( T \)-dependence of \(^{101}\text{Ru-NQR frequency which was precisely measured on a pure single crystal has detected an anomaly associated with the hidden order. Also } \nu_Q(2)(T) \) turned out to follow the \( T \)-dependence of the in-plane lattice parameter at least in the \( T \)-range between 4 and 45 K. An analysis based on the microscopic charge distribution will be desired.

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