

Nature of distributed two-fold ordering in URu₂Si₂

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Abstract. In previous ²⁹Si NMR basal-plane field rotation measurements, a weak component of two-fold broadening has been identified in the hidden-order (HO) state of URu₂Si₂. In addition, it has been revealed that the amplitude of two-fold ordering is distributed, a possible connection with imperfections in the single-crystal specimen used. In the present report, possible mechanisms for distributed two-fold ordering are discussed. As candidates, the effects of imperfections on the dotriacontapolar and hexadecapolar ordered states are considered.

1. Introduction

The nature of the second order phase transition at $T_0 \sim 17.5$ K in the heavy fermion compound URu₂Si₂ remains unclear up to now [1, 2, 3]. Since the order parameter of this transition has not ever been clearly identified, such order has been termed “hidden order” (HO) [4]. Owing to the tetragonal crystal structure of URu₂Si₂ (space group $I4/mmm$) [1], the physical properties of the disordered, *i.e.* paramagnetic, state of this compound exhibit fourfold rotational symmetry in the basal (001) plane. Based on in-plane anisotropy measurements of the torque magnetic susceptibility and on cyclotron resonance data, the fourfold symmetry has been reported to be spontaneously broken below T_0 , where a twofold rotationally symmetric state has been found to appear [5, 6]. Elastoresistance measurements also indicate an orthorhombic distortion along the [110] direction at T_0 [7]. As a consequence of domain formation, the magnitude of the twofold symmetric ordering depends strongly on sample size and can only be detected in susceptibility measurements on very small (nearly mono-domain) samples [5]. On the other hand, orthorhombic distortion appears only in high purity samples with very low residual resistivity (relative resistance ratio between 300 K and 2 K: RRR ~ 670), indicating that the twofold anisotropy seems to depend not only on sample size but also on sample quality [8].

In a previous report [9], the magnitude of twofold susceptibility anisotropy below T_0 in URu₂Si₂ has been estimated by means of ²⁹Si NMR line broadening, which does not depend explicitly on sample size. From the latter analysis the degree of twofold anisotropy in a sample with RRR ~ 70 was estimated to be 15 times smaller than that determined via static susceptibility measurements on a much smaller sample [5]. Subsequently, a detailed analysis of the line broadening [10] showed the two-fold hyperfine field amplitudes to be widely distributed. In addition, two-fold hyperfine field amplitudes appeared to be distributed around the NMR shift of the four-fold state. It may be possible that the two-fold nature could even disappear in a purer sample. Recently, we have found that the linewidth results can also be reproduced with an RKKY broadening model if two-fold magnetic impurity centers are distributed at 0.1 \sim 1.0%



of U sites [11]. In this description, over $\sim 99\%$ of U sites have four-fold symmetry. This may not be surprising, since the previously observed two-fold behavior did not appear to reflect the principal order parameter. Thus, the magnitude of it depends on sample quality, whereas the specific heat anomaly at the hidden order transition is rather insensitive indicating that the hidden order itself is well developed in lower-quality samples.

In this report, we probe the origins of distributed two-fold hyperfine fields. Specifically, we consider possible two-fold states induced by crystal imperfections in cases of multipolar ordering such as dotriacontapole or hexadecapole states.

2. Experimental

Experimental details have been presented and discussed in a previous report [9]. Single crystals were grown using the Czochralski method in a tetra-arc furnace under an argon gas atmosphere, as previously described [12]. A single crystal sample with a nearly perfect cylindrical shape ($1\text{ mm } \phi \perp [001] \times 3\text{ mm} \parallel [001]$), with narrow facets on the (110) planes, was used. Since the cross-section of the sample through the basal plane is nearly a perfect circle, no demagnetization effects need to be considered. High sample purity was confirmed by a residual resistivity of $\sim 5\text{ }\mu\Omega\text{cm}$ (RRR ~ 70). The resistivity was measured on a piece cut ($2 \times 0.5 \times 0.5\text{ mm}^3$) from the same single crystal used for NMR measurements. As pointed out previously [12], there is a distribution of RRR values in a large single crystal. As a consequence the measured value 70 should be regarded as an average RRR value for the NMR sample. It should be noted that URu_2Si_2 single crystals with RRR > 50 are already high quality single crystals in the usual sense [12], thus X-ray Laue diffraction and EPMA measurements cannot be used for evaluating the defect density in single crystal samples with RRR > 50 .

Measured on the same piece as used for the resistivity, the T -dependence of the static magnetic susceptibility χ is almost identical with that of a very high quality sample with RRR > 600 . No trace of ferromagnetic or antiferromagnetic long-range order was detected down to 2 K.

The natural abundance of the NMR isotope ^{29}Si ($I = 1/2$, gyromagnetic ratio $\gamma_{29}/2\pi = 0.84577\text{ kHz/Oe}$) is only 4.7%. This has prevented highly accurate Si NMR measurements in URu_2Si_2 up to now. For the present study, a single crystal sample with a 53% enriched ^{29}Si isotope has been prepared, improving the NMR sensitivity by a factor ~ 11 . As there are no quadrupolar interactions for $I = 1/2$ nuclei, ^{29}Si NMR spectra reflect only magnetic shift and broadening effects.

A standard pulsed NMR spectrometer was used, with magnetic field provided by a 12 T superconducting magnet in the persistent mode. NMR spectra were obtained using Fast-Fourier-Transformation (FFT) of spin-echo signals at a fixed applied magnetic field.

3. Results and Discussion

The two-fold amplitude can be defined in terms of the Knight shift anisotropy $K_{nem} \equiv K_{H\parallel[110]} - K_{H\parallel[1\bar{1}0]}$ [9], where $K_{nem} = 0$ in the four-fold state. In the case of two domains, the NMR spectra would be a superposition of two Lorentzians, one from each domain, with $K_{nem} = \text{const} > 0$. However, such a superposition cannot reproduce completely the observed spectra. Instead, the observed NMR spectra can be fitted better if a distribution of K_{nem} values is assumed in each domain [10]. As shown in Fig. 2, the no-distribution case shows a deviation between the calculation and the experiment around the peak, while the distributed case can reproduce it. For the distributed case, the distribution $g(K_{nem})$ of two-fold amplitudes K_{nem} is assumed to be [10]:

$$g(K_{nem}) = \frac{\Delta K_{nem}}{\pi(K_{nem}^2 + \Delta K_{nem}^2)}, \quad (1)$$

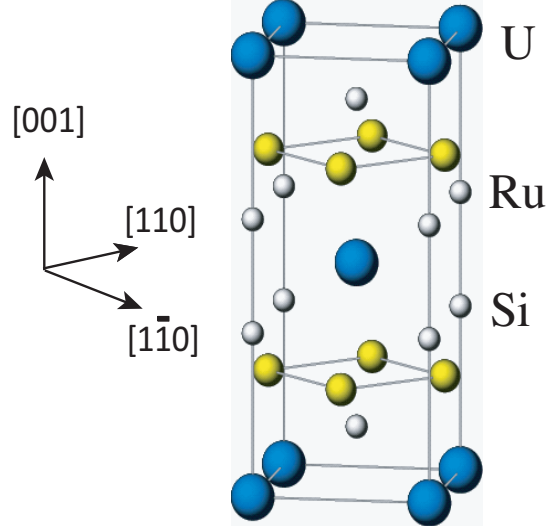


Figure 1. The crystal structure ($I4/mmm$) of URu_2Si_2 . The local symmetry of the Si is tetragonal $4mm$.

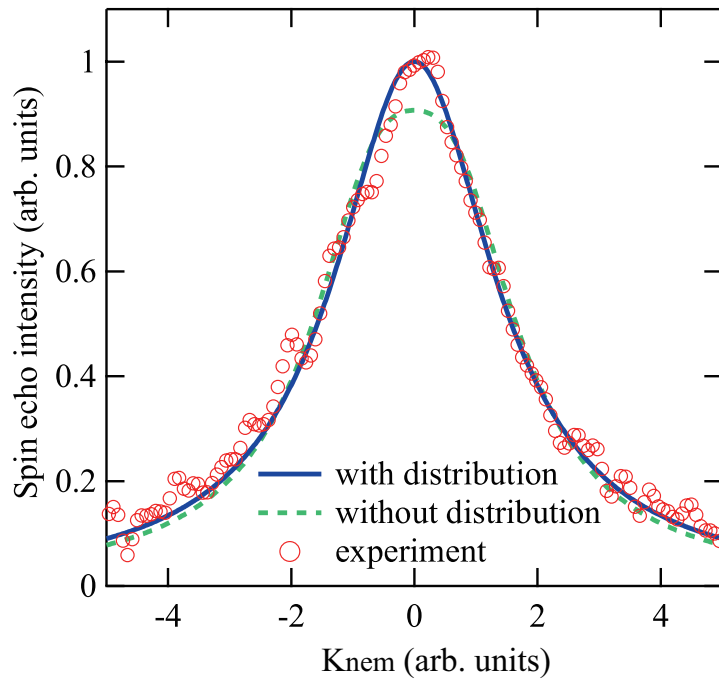


Figure 2. ^{29}Si NMR spectra with $H = 5.19$ T along the $[110]$ axis at 5 K in the hidden order state of URu_2Si_2 . Solid line is obtained using a distributed two-fold amplitude (Eq. 1) for a two-domain state. Dashed line is obtained using non-distributed (uniform) two-fold amplitude for a two-domain state.

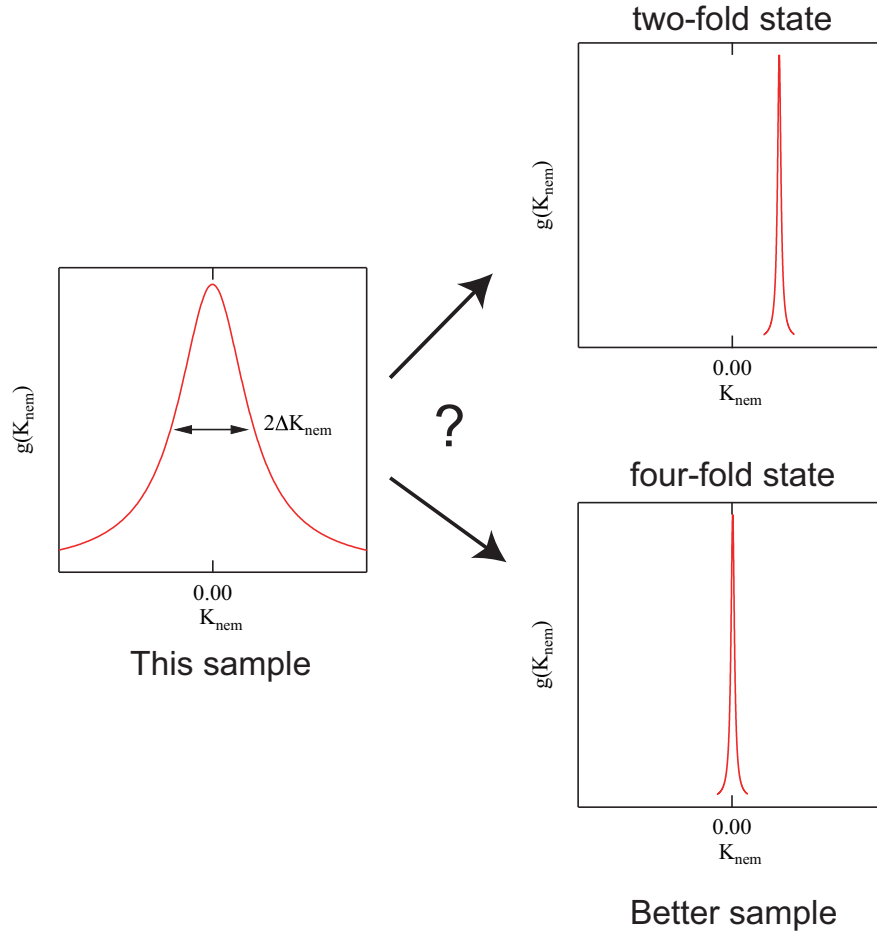


Figure 3. In the present sample, it seems that the two-fold amplitude K_{nem} is distributed around zero with the width ΔK_{nem} (left figure). In a better sample, ΔK_{nem} would be smaller (right figures). However, it is not clear whether the center position would be $K_{nem} = 0$ (four-fold state) or $K_{nem} > 0$ (two-fold state) in a better sample up to now.

where ΔK_{nem} is the distribution range of two-fold amplitudes. Also, $g(K_{nem})$ seems to have a peak at $K_{nem} = 0$ in the present sample. If ΔK_{nem} becomes zero under this situation in a better sample, there would be no two-fold amplitude, corresponding to a four-fold ordered state. At the present stage, we note that it is not clear whether the peak would locate at $K_{nem} = 0$ (four-fold state) or $K_{nem} > 0$ (two-fold state) in a better sample that exhibits intrinsic properties. In actual fact, a previous study implied that the two-fold state is prominent in a better sample [8].

Next, we discuss possible mechanisms for distributed two-fold hyperfine fields. Such hyperfine fields may appear perhaps due to distributions of impurities, dislocations or local stress (IDLS), *i.e.* two-fold states would be induced when the hidden order is broken by IDLS. In the four-fold paramagnetic state, such a two-fold state due to IDLS has not been identified [9], thus such a two-fold state may reflect the hidden order. Recently, dotriacontapolar [13] and hexadecapolar [14] order have been proposed as candidates for the hidden order parameter. These two possibilities are discussed below.

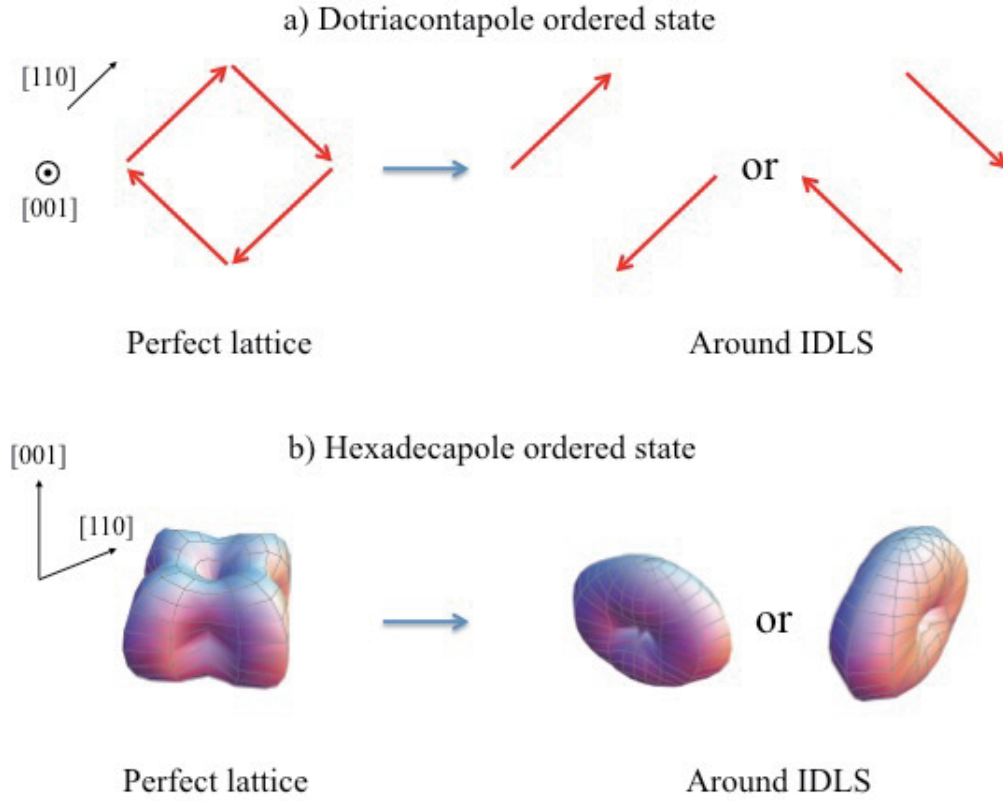


Figure 4. Schematic view of impurities, dislocations and local stress (IDLS) effects. a) Dotriacontapole case: a small moment may appear at the U site along the $[110]$, $[1\bar{1}0]$, $[\bar{1}10]$ or $[\bar{1}\bar{1}0]$ directions with the same population at the U site in a perfect lattice (left). Although the two-fold state appears at U sites locally, this state is effectively four-fold. Consequent to IDLS, two types of two-fold sublattices could appear, which could generate two domains (right). b) Hexadecapole case: this shape represents the density of electrons around the U site. The order parameter is locally four-fold in the perfect lattice (left). Owing to IDLS, two type of quadrupolar ordering could appear which could cause the two domains (right). As an example, O_{22} -type quadrupolar order is presented here.

3.1. Dotriacontapole scenario

In the dotriacontapolar state, a tiny pseudo-spin moment is induced at the U site along the $[110]$ direction antiferromagnetically [13]. In this scenario, a two-fold state appears locally; however, owing to degenerate states with ordered moments along $[110]$, $[1\bar{1}0]$, $[\bar{1}10]$ and $[\bar{1}\bar{1}0]$ at the U site with equal populations, the NMR spectra keep four-fold symmetry. Through IDLS this equilibrium could be broken, inducing a preference for certain sublattices which show a two-fold symmetry [Fig. 4a)]. In addition, appearance of local antiferromagnetic dipolar ordering through IDSL would be possible, since the energy levels of dotriacontapolar and dipolar ordered

states are quite similar and can easily be reversed by *e.g.* pressure [13, 15]. In a perfect crystal, if a mono-domain can remain dominant, the two-fold state case in Fig. 3 will be observed, while a four-fold case will be observed if all domains have the same population. Therefore, a two-fold amplitude may depend strongly on sample conditions. Considering that ordered moments perpendicular to an applied field may not affect K_{nem} , both states in Fig. 3 could be realized for the dotriacontapole case.

3.2. Hexadecapole scenario

In the hexadecapole state, four-fold symmetry is locally preserved at the U site [14]. However, when uniaxial stress along the [110] or [100] directions is applied, the two-fold quadrupolar states O_{xy} and $O_{x^2-y^2}$, respectively, could be induced [14]. Thus, it is expected that similar behavior would occur around impurities and dislocations [Fig. 4b)]. If a finite $K_{nem} > 0$ were intrinsic (the two-fold state case in Fig. 3), then the hexadecapole scenario would not occur. Thus, in a better sample the four-fold case in Fig. 3 would be observed for the hexadecapole scenario.

It should be noted that the detailed mechanism for a Lorentzian-like distribution of two-fold hyperfine fields is not understood at present. The above scenarios just indicate possible origins for such a distribution. The two-fold amplitude may well depend on the type of ordering and on imperfections. Recently, we have found that two-fold magnetic centers at $0.1 \sim 1\%$ of U sites could reproduce the NMR data based on an RKKY transferred HF coupling model [11]. The proposed two-fold states in Fig. 4 could correspond to these magnetic centers. A crucial difference between the dotriacontapole and hexadecapole ordering is that time-reversal symmetry is broken in the dotriacontapole state, whereas it is not broken in the hexadecapole state. Up to now, however, it is still not clear whether time reversal symmetry is broken or not in the HO state of URu₂Si₂.

4. Conclusion

Based on a detailed analysis of ²⁹Si NMR linewidths in the hidden order state of URu₂Si₂, the two-fold hyperfine fields at Si sites are found to be distributed. The effect of crystalline imperfections on dotriacontapolar and hexadecapolar multipolar ordering has been discussed as the possible origin of distributed two-fold hyperfine fields. In practice, we suggest that a two-fold state could appear around the imperfections in these states. To distinguish between these two types of ordering, sample quality dependence of the two-fold hyperfine fields as well as determination of time reversal symmetry would be useful.

Acknowledgments

The high quality sample for our measurements was prepared by T.D. Matsuda, Y. Haga and Z. Fisk, which is greatly appreciated. We thank K. Kubo for preparing the figures of hexadecapole and quadrupole ordering in Fig. 4b). We are grateful for stimulating discussions with T. Shibauchi, H. Ikeda, M.-T. Suzuki, Y. Matsuda, D. Aoki, F. Bourdarot, J. A. Mydosh, H. Amitsuka and J. Flouquet. A part of this work was supported by a Grant-in-Aid for Scientific Research on Innovative Areas Heavy Electrons (No. 20102006 and No. 20102007) by the MEXT, and the REIMEI Research Program of JAEA.

References

- [1] Palstra T T M, Menovsky A A, van den Berg J, Dirkmaat A J, Kes P H, Nieuwenhuys G J and Mydosh J A 1985 *Phys. Rev. Lett.* **55** 2727.
- [2] Schlätz W, Baumann J, Pollit B, Rauchsvalbe U, Mayer H M, Ahlheim U and Bredl C D *Z. Phys. B Condensed Matter* **62** 171.

- [3] Maple M B, Chen J W, Dalichaouch Y, Kohara T, Rossel C, Torikachvili M S, McElfresh M W and Thompson J D 1986 *Phys. Rev. Lett.* **56** 185.
- [4] Tripathi V, Chandra P and Coleman P 2007 *Nature Phys.* **3** 78.
- [5] Okazaki R, Shibauchi T, Shi H J, Haga Y, Matsuda T D, Yamamoto E, Onuki Y, Ikeda H and Matsuda Y 2011 *Science* **331** 439.
- [6] Tonegawa S, Hashimoto K, Ikada K, Lin Y-H, Shishido H, Haga Y, Matsuda T D, Yamamoto E, Onuki Y, Ikeda H, Matsuda Y and Shibauchi T 2012 *Phys. Rev. Lett.* **109** 036401.
- [7] Riggs S C, Shapiro M C, Maharaj A V, Raghu S, Bauer E D, Baumbach R E, Giraldo-Gallo P, Wartenbe M and Fisher I R 2015 *Nature Comms.* DOI: 10.1038/ncomms7425.
- [8] Tonwgawa S, Kasahara S, Fukuda T, Sugimoto K, Yasuda N, Tsuruhara Y, Watanabe D, Mizukami Y, Haga Y, Matsuda T D, Yamamoto E, Onuki Y, Ikeda H, Matsuda Y and Shibauchi T 2014 *Nature Comms.* DOI: 10.1038/ncomms5188.
- [9] Kambe S, Tokunaga Y, Sakai H, Matsuda T D, Haga Y, Fisk Z and Walstedt R E 2013 *Phys. Rev. Lett.* **110** 246406. See also the supplement for this paper.
- [10] Kambe S, Tokunaga Y, Sakai H and Walstedt R E 2015 *Phys. Rev. B* **91** 035111.
- [11] Walstedt R E, Kambe S, Tokunaga Y and Sakai H 2016 *Phys. Rev. B* **93** 045122.
- [12] Matsuda T D, Hassinger E, Aoki D, Taufour V, Knebel G, Tateiwa N, Yamamoto E, Haga Y, Onuki Y, Fisk Z and Flouquet J 2011 *J. Phys. Soc. Jpn.* **80** 114710.
- [13] Ikeda H, Suzuki M T, Arita R, Takimoto T, Shibauchi T and Matsuda Y 2012 *Nature Phys.* **8** 528.
- [14] Kusunose H and Harima H 2011 *J. Phys. Soc. Jpn.* **80** 084702.
- [15] Hassinger E, Knebel G, Izawa K, Lejay P, Salce B and Flouquet J 2008 *Phys. Rev. B* **77** 115117.