# Quadrupolar ordering of $5f$ electrons in $UCu_2Sn$

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A huge softening of the transverse elastic modulus $C_{66}$ has been found in $UCu_2Sn$ around a phase transition point at $\sim 16$ K. In addition to the elastic moduli, the specific heat and x-ray diffraction were measured for polycrystals and single crystals in order to elucidate the origin for the transition. All anomalies obtained in the thermodynamic properties were analyzed by assuming a localized $5f^2$ configuration in the hexagonal symmetry. It is revealed that the transition originates from a quadrupolar ordering of the non-Kramers ground doublet $\Gamma_5$.

Extensive searches have been carried out for systems in which multipolar interactions are predominant. Total understanding of magnetic properties arising from spins and orbitals of electrons provides us with the prospect of finding a paradigm in magnetism such as the quadrupolar Kondo effect,[1] for instance. Many systems exhibiting orbital or multipolar ordering have been found in rare-earth compounds.[2] However, a wave function of $5f$ electrons usually spreads out wider in space than that of $4f$ electrons, and the stronger hybridization between the $5f$ and conduction electrons leads to an itineracy of the $5f$ electrons. Only a few actinide compounds, such as $URu_2Si_2$,[3] $UPd_3$,[4] and UNiSn,[5] have been proposed to undergo multipolar transitions. In $URu_2Si_2$, antiferroquadrupolar (AFQ) ordering was pointed out as a most likely candidate which explains its peculiar magnetism.[3] An AFQ ordered structure of $UPd_3$ was revealed by a neutron diffraction technique.[4] However, due to two different U sites in the double-hexagonal close-packed crystal structure, the electronic property of $UPd_3$ seems to always involve a mixed contribution from different crystal-electric-field (CEF) excitations for hexagonal and cubic symmetries. On the other hand, in cubic UNiSn possessing a single U site, ferroquadrupolar (FQ) ordering occurs concurrently with a first-order antiferromagnetic (AFM) transition. The phase transition mechanism was clearly explained by Akazawa *et al.*[5] using the CEF level scheme proposed by Aoki *et al.*[6] However, difficulty in growing a single crystal has prevented us from further experiments on anisotropy of the electronic property. In this article, we will show that $UCu_2Sn$, which has a single U site in a hexagonal structure of $ZrPt_2Al$ type (space group $P6_3/mmc$),[7] substantially undergoes the quadrupolar ordering.

In $UCu_2Sn$ with lattice parameters of $a=4.457$ Å and $c=8.713$ Å at room temperature, constituent atoms are stacked in layers perpendicular to the hexagonal $c$ axis with a sequence of ... Sn, Cu, U, Cu ... Each layer consists of only one element so that the U layer is sandwiched by the Cu layers. The nearest distance between U ions is $d_{\text{U-U}} \simeq 4.46$ Å, far beyond Hill's limit $d_{\text{Hill}} \simeq 3.5$ Å. The distances between the U ions and ligands are $d_{\text{U-Cu}} \simeq 2.87$ Å and $d_{\text{U-Sn}} \simeq 3.37$ Å. Therefore, hybridization is expected between $5f$ and other electrons from ligands although a direct overlap of $5f$ wave functions is unlikely in the U layer. $UCu_2Sn$ exhibits an anomaly at 16.6 K in both the specific heat and magnetic susceptibility.[7] The anomaly was attributed to an AFM order because a spin-flop-like change in the magnetization curve was also observed at 23.5 T in the ordered state.[7] As for the transport property, the abrupt increase of the electrical resistivity below 16.6 K was interpreted in terms of superzone gap formation due to the AFM order.[8] However, recent Mössbauer[9] and NMR (Ref. 10) spectroscopies inferred the absence of a hyperfine field at Sn and Cu sites, suggesting that the ordering is not of simple AFM. Furthermore, neutron diffraction[8] detected no magnetic reflection for both polycrystals and single crystals. We can expect another origin for the phase transition at 16.6 K than AFM order.

The magnetic susceptibility of $UCu_2Sn$ above 150 K follows the Curie-Weiss law with an effective magnetic moment of $\mu_{\text{eff}}=(3.0-3.6)\mu_B/\text{U}$ corresponding to $5f^2$ or $5f^3$ configurations, which suggests a localized nature of the $5f$ electrons at least above 150 K. If the $5f$ electrons in this compound are nearly localized even at low temperatures and retain the $5f^2$ configuration with total angular momentum $J=4$, the quadrupolar degeneracy is expected to exist in the ground state since in the hexagonal CEF the $5f^2$ state splits into seven eigenstates, three singlets $\Gamma_1$, $\Gamma_3$, and $\Gamma_4$ and three non-Kramers doublets $2\Gamma_5$ and $\Gamma_6$ with degenerate quadrupoles, where $\Gamma_i$ denotes the irreducible representation for the $6/mmm$ point group. Thus, the unusual transition is possibly understood in the framework of the quadrupolar ordering. In order to determine whether the transition in $UCu_2Sn$ originates from spin or orbital ordering, we measured specific heat, elastic moduli, and x-ray diffraction. Especially, the elastic moduli, which are the strain-quadrupolar susceptibility, are sensitive to detect the quadrupolar ordering.[5,11,12]

Details of the sample preparation for the polycrystals and single crystals were reported elsewhere.[7,8] Powder x-ray diffraction confirmed that the polycrystals were in a single phase with hexagonal $ZrPt_2Al$ structure. Electron-probe microanalysis for the single crystal detected an impurity phase

 

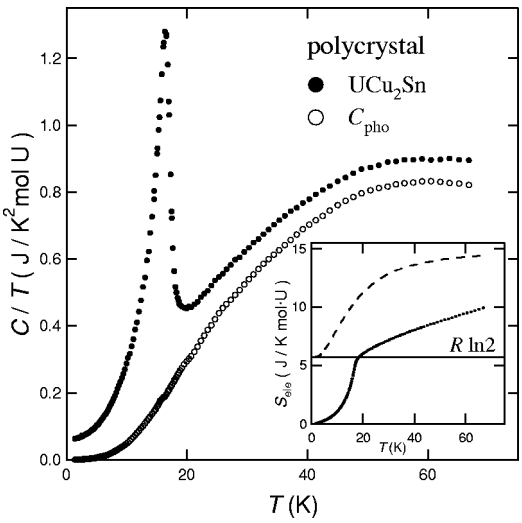


FIG. 1. The specific heat of $UCu_2Sn$ and its phonon contribution are shown by solid and open circles, respectively. The electronic entropy is shown by solid circles in the inset. The dashed curve, which is shifted vertically by $R \ln 2$, was calculated using the CEF excitation proposed in this work.

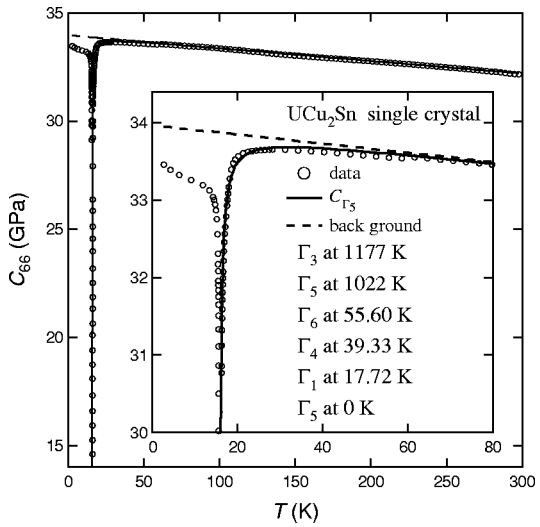


FIG. 2. Temperature dependence of $C_{66}$. The solid curve and the dashed line show the best fit of $C_{\Gamma_5}$ and the background stiffness, respectively. The inset demonstrates the same data in an expanded scale and the CEF level scheme from the ground doublet $\Gamma_5$ to the fifth excited singlet $\Gamma_3$ with corresponding excitation energy. The level scheme was obtained by using the CEF parameters listed in Table I.

of UCuSn at $\sim 4\%$ of the host crystal. A polycrystal of the isomorphic reference material $ThCu_2Sn$ without $5f$ was also prepared. Molar specific heat $C$ was measured as a function of temperature $T$ from 1.4 to 70 K for polycrystals of $UCu_2Sn$ and $ThCu_2Sn$ using an adiabatic calorimeter. The ultrasonic velocity $v$ at $\sim 9$ MHz, which is the fundamental frequency of our transducers, was measured by a pulse-echo phase-comparison method. The elastic modulus $C_{ii}$ was calculated using the equation $C_{ii}=\rho v^2$ with the room-temperature value of mass density $\rho = 10.720$ g/cm$^3$.

In Fig. 1, $T$ dependence of $C/T$ is shown by solid circles for a polycrystal of $UCu_2Sn$. A clear anomaly of mean-field type was observed around the transition temperature $T_Q = 16.5$ K, where $T_Q$ was defined as the temperature at which $C$ attains a peak. The value of $C/T = 63$ mJ/K$^2$ mol observed at 1.40 K agrees with the reported value.[7,8] The mean-field-type anomaly suggests that the transition is of second order and a long-range interaction is responsible for the transition. A multipole-multipole interaction usually has a longer correlation range than a spin-spin interaction. We estimated the phonon contribution $C_{\rm pho}$ to specific heat of $UCu_2Sn$ using the specific heat $C_{\rm Th}$ of $ThCu_2Sn$. The data of $C_{\rm Th}$ can be fitted very well to $C_{\rm Th}=\gamma T+\beta T^3$ between 1.40 and 4.79 K with the values of $\gamma = 2.795$ mJ/K$^2$ mol and $\beta = 0.239$ mJ/K$^4$ mol. The phonon contribution $C_{\rm pho}$ shown by open circles in Fig. 1 was calculated by subtracting $\gamma T$ from $C_{\rm Th}$. The correction for difference in Debye temperatures between U and Th compounds due to the difference in mass has not been made because of the small mass difference of $\sim 1.2\%$. The electronic contribution $S_{\rm ele}$ to the entropy shown in the inset was calculated by integration of the difference between $C_{\rm pho}/T$ and $C/T$. At $T_Q = 16.5$ K, $S_{\rm ele}$ attains $R \ln 2$ regardless of the ambiguity in the $C_{\rm pho}$ estimation, where $R$ is the gas constant. The entropy clearly reveals that there exist at least two states below an energy scale of $\sim 16$ K, strongly suggesting that a doublet is the ground state in the nonordered phase.

If the ground state is a non-Kramers doublet and there is an interaction between the ground doublets at different U ions, a remarkable softening in an elastic modulus must be observed at a finite temperature[12] due to a structural instability originating from the quadrupolar ordering or cooperative Jahn-Teller effect.[13] We have measured longitudinal $C_{11}, C_{33}$ and transverse $C_{44}, C_{66}$ modes of the single crystal, where $C_{66}$ and $(C_{11}-C_{12})/2$ as well as $C_{44}$ and $C_{55}$ are degenerate in a hexagonal symmetry.[12] As mentioned above, $\Gamma_5$ and $\Gamma_6$ may exist in $UCu_2Sn$. One can easily judge which of $\Gamma_5$ and $\Gamma_6$ is the ground doublet by looking at the $T$ dependence of $C_{66}$ and $C_{44}$, since $C_{66}$ and $C_{44}$ are the linear responses to $\varepsilon_{\Gamma_5}$ $[=\varepsilon_{xy}$ and $\varepsilon_{xx}-\varepsilon_{yy}(\equiv\varepsilon_t)]$ and $\varepsilon_{\Gamma_6}(=\varepsilon_{yz}$ and $\varepsilon_{zx})$ strains, respectively, and $\Gamma_5$ and $\Gamma_6$ directly couple to $\varepsilon_{\Gamma_5}$ and $\varepsilon_{\Gamma_6}$. As shown in Fig. 2, a significant softening of $C_{66}$ with more than 57% reduction of the stiffness was successfully observed by controlling temperature carefully within the 1 mK fluctuation.[14] The softening was also confirmed by the direct measurement of a change in the time interval between the drive pulse and the first echo. The echo pulses for $C_{66}$ faded away between 15.58 and 15.96 K due to the huge ultrasonic attenuation diverging toward $T_Q$. With decreasing $T$, $C_{66}$ starts to soften around 24 K and attains a minimum at $\sim 15.7$ K. The minimum point is lower by 1 K than $T_Q$ determined from the peak of the specific heat. This may be due to the difference in sample quality between polycrystals and single crystals. A small anomaly detected at $\sim 61$ K in $C_{66}$ and $C_{11}$ comes from the magnetic transition of the UCuSn impurity.[8] Such a large softening of the lattice cannot be explained as an elastic anomaly only from the antiferromagnetic transition. It is understood as the quadrupolar ordering in the discussion below. In contrast with the large anomaly in $C_{66}$, other anomalies around $T_Q$ in elastic moduli $C_{11}$, $C_{33}$, and $C_{44}$ presented in Fig. 3 are smaller than 1% although their $T$ dependence is characteristic of the CEF effect on elastic moduli.[15] In principle, $C_{11}$ should show a

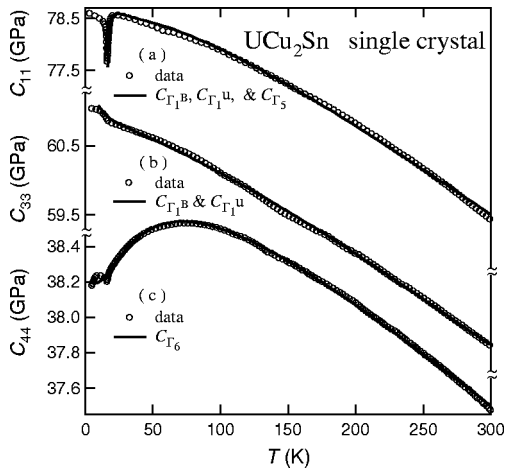


FIG. 3. (a) $C_{11}$ vs $T$, (b) $C_{33}$ vs $T$, and (c) $C_{44}$ vs $T$. The solid curves demonstrate the best fits.

large softening since it is a mixed mode of $C_{\Gamma_5}$, $C_{\Gamma_1^B}$, and $C_{\Gamma_1^u}$, where $C_{\Gamma_1^B}$ and $C_{\Gamma_1^u}$ are responses to $\varepsilon_{\Gamma_1^B}=\varepsilon_{xx}+\varepsilon_{yy}+\varepsilon_{zz}$ and $\varepsilon_{\Gamma_1^u}=(3\varepsilon_{zz}-\varepsilon_{\Gamma_1^B})/\sqrt{3}$. The reason for the small anomaly in $C_{11}$ may be that we could detect only $C_{\Gamma_1}$ components of the phase signal in a echo pulse of the $C_{11}$ mode in the vicinity of $T_Q$ because the $C_{\Gamma_5}$ component rapidly fades out due to the colossal attenuation and then the $C_{\Gamma_1}$ components with little attenuation predominate in the echo.

The remarkable softening of $C_{66}$ is regarded as clear evidence that the transition originates from the instability of the ground doublet $\Gamma_5$ which has the degenerate quadrupoles $O_{xy}$ and $O_2^2$. To confirm this idea theoretically, we analyzed the elastic moduli using the strain susceptibility $\chi_s$.[15] As is obvious in Fig. 2, $C_{66}$ is well restored to the background stiffness below $T_Q$. Thus, we can assume a linear coupling between a strain and an order parameter[16] across the second-order transition, so that we consider the effective Hamiltonian $H$:

$$H=H_{\mathrm{CEF}}-H_{\mathrm{ME}}-g'_{\Gamma_i}\langle O_{\Gamma_i}\rangle O_{\Gamma_i},$$

$$H_{\mathrm{CEF}}=B_2^0O_2^0+B_4^0O_4^0+B_6^0O_6^0+B_6^6O_6^6, \tag{1}$$

$$\begin{aligned}H_{\mathrm{ME}}=&g_{\Gamma_5}(O_{xy}\varepsilon_{xy}+O_2^2\varepsilon_t)+g_{\Gamma_6}(O_{yz}\varepsilon_{yz}+O_{zx}\varepsilon_{zx})\\&+g_{\Gamma_1^u}O_2^0\varepsilon_{\Gamma_1^u}+(g^{\alpha}_{\Gamma_1^B}O_2^0+g^{\beta}_{\Gamma_1^B}O_4^0+g^{\gamma}_{\Gamma_1^B}O_6^0\\&+g^{\delta}_{\Gamma_1^B}O_6^6)\varepsilon_{\Gamma_1^B},\end{aligned}$$

where $g'$, $O$, $B$, and $g$ are a quadrupole-quadrupole coupling constant, an operator equivalent, a CEF parameter, and a multipole-strain coupling constant, and $\langle O_{\Gamma_i}\rangle$ represents the thermal average of $O_{\Gamma_i}$. We take account of higher-order multipoles $O_4^0$, $O_6^0$, and $O_6^6$ in the $C_{\Gamma_1^B}$ calculation since the operator $J^2$ does not give a $T$ dependence.[15] The coupling between these multipoles is omitted because it is not very important for the purpose of this paper to clarify the origin of the transition. We performed a fitting to all elastic data for the nonordered state between $T_Q$ and room temperature using the equation

$$C_{\Gamma_i}=\frac{-N_0g_{\Gamma_i}^2\chi_s}{1-g'_{\Gamma_i}\chi_s}+C_0, \tag{2}$$

where $N_0=1.334\times10^{28}$ m$^{-3}$ is the number density of U ions per unit volume at room temperature, and the linear $T$ dependence of the background stiffness was assumed as $C_0=a+bT$. The fitting parameters are $B$, $g$, $g'$, $a$, and $b$. The reproduction of longitudinal modes was performed by using a combination of $C_{\Gamma_1^B}$ and $C_{\Gamma_1^u}$ for $C_{33}$ and that of $C_{\Gamma_1^B}$, $C_{\Gamma_1^u}$, and $C_{\Gamma_5}$ for $C_{11}$, respectively. The parameters $B$, $g$, and $g'$ were self-consistently determined for all modes. The best fits are shown by solid curves in Figs. 2 and 3. The theoretical curves well reproduce all the data above $T_Q$ with the parameters listed in Tables I and II. The CEF level scheme corresponding to $B$'s in Table I is shown in the inset of Fig. 2. As a check of this analysis, using the fixed CEF parameters in Table I, we calculated the electronic contribution $S_{\mathrm{ele}}$ to the entropy for the nonordered state. The theoretical $S_{\mathrm{ele}}$ shown by a dashed curve in the inset of Fig. 1 is gradually getting closer to the experimental data with increasing $T$, which does not rule out the validity of the calculation. As a consequence, the analysis has evidently confirmed that $\Gamma_5$ is the ground state of $UCu_2Sn$ above $T_Q$. Moreover, it is confirmed that the transition originates from the quadrupolar ordering since the condition $D$ $(\equiv|g'C_0/g^2N_0|)\gg1$ is achieved in the $C_{66}$ mode as shown in Table II, which satisfies a criterion in discriminating the quadrupolar ordering from the cooperative Jahn-Teller transition.[13] The analysis also strongly suggests a ferroquadrupolar-type ordered structure below $T_Q$ because of the positive value of the quadrupole-quadrupole coupling constant $g'_{\Gamma_5}\simeq0.18$ K.

In case of a ferroquadrupolar transition, a structural change should be observed macroscopically due to the emer-

TABLE I. The CEF parameters for the best fit.

| $B_2^0$ (K) | $B_4^0$ (K) | $B_6^0$ (K) | $B_6^6$ (K) |
|---|---|---|---|
| $1.682\times10$ | $-6.100\times10^{-2}$ | $-1.720\times10^{-3}$ | $2.257\times10^{-1}$ |

TABLE II. Obtained parameters $g_{\Gamma_i}$ (K), $g'_{\Gamma_i}$ (K), $a$ (GPa), $b$ ($10^{-3}$GPa/K), $D$, and elastic modes corresponding to operators (Op.). $g_{\Gamma_1^u}$ and $g^{\alpha}_{\Gamma_1^B}$ are presented as the numerals with superscripts $u$ and $B$, respectively.

| Op. | $O_{xy}$ | $O_{yz}$ | $O_2^0$ | $O_4^0$ | $O_6^0$ | $O_6^6$ |
|---|---|---|---|---|---|---|
| $\lvert g_{\Gamma_i}\rvert$ | 8.632 | 130.4 | $51.67^u$ $44.47^B$ | 0.341 | 0.010 | 1.021 |
| $g'_{\Gamma_i}$ | 0.177 | $-1.080$ | $-0.65$ | – | – | – |

| Mode | $C_{66}$ ($\Gamma_5$) | $C_{44}$ ($\Gamma_6$) | $C_{33}$ ($\Gamma_1^B$,$\Gamma_1^u$) | $C_{11}$ ($\Gamma_1^B$,$\Gamma_1^u$,$\Gamma_5$) |
|---|---|---|---|---|
| $a$ | 33.97 | 40.04 | 61.51 | 80.04 |
| $b$ | $-5.885$ | $-6.752$ | $-11.79$ | $-16.45$ |
| $D$ | 437 | 13.8 | $\sim10^2$ | $\sim10^2$ |

gence of the spontaneous strain ($\varepsilon_{\Gamma_5}$ for $UCu_2Sn$) as is the case of the ferroquadrupolar UNiSn.[5] In spite of the repeated x-ray diffraction experiments on polycrystalline $UCu_2Sn$ between 4.2 K and room temperature, we could observe neither a broadening of a diffraction peak indicating FQ ordering nor superlattice reflection indicating AFQ ordering. There is no direct evidence which reveals whether the ordering is of ferroquadrupole or antiferroquadrupole at present. However, the possible reason for no indication of the structural change is mainly due to the small $g_{\Gamma_5}$ for $UCu_2Sn$, which is smaller by one order of magnitude than that for UNiSn. In the framework of our theoretical model, we calculated magnitudes of the order parameter and corresponding strain in the ordered state. The result has revealed that the plausible order parameter is the quadrupole $O_{xy}$ rather than $O_2^2$ and the magnitude of the spontaneous strain $\varepsilon_{xy}$ is about $5.6\times10^{-4}$ which is slightly less than our experimental resolution, where the relation $|\varepsilon_{xy}|=N_0 k_B g_{\Gamma_5}\langle O_{xy}\rangle/C_0$ (Ref. 15) was used with $g_{\Gamma_5}\simeq 8.6$ K, $\langle O_{xy}\rangle\simeq 12$ at 0 K, and $C_0\simeq 34$ GPa. Details of the calculation for the ordered state and a refinement of the CEF parameters will be published elsewhere with the data measured in the magnetic fields.

Let us consider the compatibility between the idea of the ferroquadrupolar ordering and the actual properties in the ordered state of this compound. The absence of hyperfine field at the Sn and Cu sites and no magnetic reflection in the neutron diffraction are naturally understood by admitting that the transition originates from the quadrupolar ordering. The spin-flop-like change in the magnetization curve at 23.5 T may be attributed to level crossing due to an effect from the Zeeman energy since the first, second, and third excited levels are closely situated above the ground state. The magnetic energy for 23.5 T is at least comparable to the excitation energy of the first excited level. The semiconductorlike upturn in the resistivity below $T_Q$ is probably due to the emergence of the spontaneous strain which modifies electron hybridization.

The discussion above is valid when the $5f$ electrons are nearly localized even at low temperatures. Let us examine a localized regime in which the $\Gamma_5$ ground state is formed in a hexagonal CEF. It should be noted that the $\Gamma_5$ wave function is extended in the $xy$ plane and the population of the ground state is exponentially increased with decreasing $T$. Thanks to the lattice structure of $UCu_2Sn$ in which each layer consists of only one element, the $5f$ electrons tend to be confined in the U layer and to lose a chance of mixing with the electrons from Sn and Cu as $T$ is decreased. Moreover, since the nearest U-U distance is far beyond Hill's limit, the direct overlap is not expected among the $\Gamma_5$ orbitals. Consequently, such structural and electronic conditions of $UCu_2Sn$ tend to allow the $5f$ electrons to preserve the localized nature at low temperatures. It is concluded, therefore, that the phase transition at $\sim 16$ K in $UCu_2Sn$ originates from the quadrupolar ordering of the ground-state non-Kramers doublet $\Gamma_5$ and that the most plausible ordering is of ferroquadrupolar type.

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