Spontaneous strain due to ferroquadrupolar ordering in UCu₂Sn

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The ternary uranium compound UCu₂Sn with a hexagonal ZrPt₂Al-type structure shows a phase transition at 16 K. We reported previously that huge lattice-softening is accompanied by the phase transition, which originates from ferroquadrupolar ordering of the ground state non-Kramers doublet Γ₅. A macroscopic strain, which is expected to emerge spontaneously, was not detected by powder X-ray diffraction in the temperature range between 4.2 and 300 K. To search the spontaneous strain, we have carried out thermal expansion measurements on a single-crystalline sample along the a, b and c axes using a capacitance technique with the resolution of 10⁻⁸. In the present experiment, we found the spontaneous $e_{xx} - e_{yy}$ strain which couples to the ground state doublet Γ₅. The effect of uniaxial pressure along the a, b and c axes on the transition temperature is also discussed.

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I. INTRODUCTION

Multipolar ordering have been intensively investigated in a number of 4f-electron compounds [1]. In the case of 5f-electron systems, however, the multipolar ordering has been reported only in a few compounds, including NpO₂, UPd₃, URu₂Si₂, UNiSn and UCu₂Sn [2]. Previously we pointed out that UCu₂Sn and UNiSn undergo ferroquadrupolar ordering at low temperatures.

The compound UCu₂Sn has a hexagonal ZrPt₂Al-type structure (space group P6₃/mmc) with the lattice parameters of $a = 4.457$ Å and $c = 8.713$ Å at room temperature. In this hexagonal structure, constituent atoms are stacked in layers perpendicular to the c axis in regular sequence of $\cdots$Sn, Cu, U and Cu$\cdots$, where all U atoms occupy equivalent sites forming a triangle lattice. Takabatake et al. found that UCu₂Sn underwent a phase transition around 16 K [3]. Afterwords, the transition was estimated to be a non-magnetic one since Mössbauer [4] and NMR [5] spectroscopies inferred the absence of a hyperfine field at Sn and Cu sites and neutron diffraction detection no magnetic reflection [6]. In our previous study on the specific heat and elastic moduli of UCu₂Sn [7], we determined the crystal electric field (CEF) parameters ($B_0^g = -6.100 \times 10^{-2}$ K, $B_0^b = -1.720 \times 10^{-3}$ K, and $B_0^c = 2.257 \times 10^{-1}$ K) and the CEF level scheme from the ground state non-Kramers doublet Γ₅ to the fifth excited state Γ₃, where Γ₁ is the irreducible representation for the $6/mmm$ point group. We also explained the reasons why the U ions formed the 5f² configuration with the total angular momentum $J = 4$ and the 5f-electrons were in the localized regime. The most prominent feature was that the transverse modulus $C_{66}$ exhibited the huge softening around $T_Q = 16$ K, which was an evidence for the ferroquadrupolar ordering of the ground state Γ₅. The modulus $C_{66}$ is the linear response to $e_{zz}$ (= $e_{xy}$ and = $e_{xx} - e_{yy}$) strain in the hexagonal lattice. Taking account of both the strain-quadrupole coupling and the quadrupole-quadrupole (q-q) coupling, we analyzed $C_{66}$ and then obtained the positive sign for the q-q coupling coefficient $g_{\Gamma_5}^q$, that is, ferroquadrupolar coupling in the ground state. To distinguish the quadrupolar ordering from the cooperative Jahn-Teller transition, we employed a non-dimensional parameter $D = |g^qC_0/g^2N_0| [11]$, where $g$ is the strain-quadrupole coupling coefficient, $C_0$ is the background value of the elastic modulus and $N_0$ is the number density of U ions per unit volume at room temperature. The obtained result $D \gg 1$ clearly indicated that the q-q coupling $g^q$ predominates over the strain-quadrupole coupling $g$ in UCu₂Sn and consequently the transition is classified as the ferroquadrupolar ordering. The ferroquadrupolar ordering must be accompanied by a macroscopic strain or distortion below $T_Q$. In the previous work [7] using the powder X-ray diffraction technique, we did not succeed in detecting any indication for the spontaneous occurrence of macroscopic strain. So we made numerical estimation by using the relation $|e_{xy}| = N_0k_Bg_5\langle Q_{xy}\rangle/C_0 [12]$ with the parameters obtained from fitting the elastic modulus, and we found that the spontaneous strain

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measured as a function of temperature $T_c$ and described elsewhere [10]. An impurity phase of UCuSn might be as small as $5.6 \times 10^{-4}$. The value was smaller than the resolution of our X-ray diffraction ($\sim 1 \times 10^{-3}$). In the present work, we have carried out the thermal expansion experiments on a single-crystalline sample by a capacitance method [13].

II. EXPERIMENTAL

A single crystal of UCu$_2$Sn was grown by a Bridgman method. The details of sample preparation was described elsewhere [10]. An impurity phase of UCuSn ($\sim 4 \%$) was detected in our single-crystalline sample of UCu$_2$Sn by the electron probe microanalysis. The sample was shaped in a rectangular parallelepiped of $2.824 \times 2.908 \times 3.288$ mm$^3$. Thermal expansion $\Delta l/l$ was measured as a function of temperature $T$ from 4.2 to 40 K with a temperature interval of 0.1 K along the $a$, $b$ and $c$ axes using a three-terminal method of capacitance measurement. Small change in length of the sample was detected by means of change in capacitance between the parallel plates with approximately 0.1 mm spacing [13]. The plates have an area of $\approx 1.55 \times 10^2$ mm$^2$. The value of $\Delta l/l$ for each axis was defined as $(l(T) - l(40K)) / l(40K)$. The $a$ and $c$ axes are referred to the international tables (space group $P6_3/mmc$) [13]. The $b$ axis is defined as perpendicular to the $a$ axis in the hexagonal $c$ plane.

III. RESULTS & DISCUSSION

Figure 1 shows temperature dependence of thermal expansion $\Delta l/l$ both for along the $a$ and $b$ axes. At high temperatures, both of $\Delta l/l$ along the $a$ and $b$ axes decrease monotonically with decreasing temperature. At low temperatures below $T_Q$, $\Delta l/l$ along the $a$ axis, that is $\Delta a/a$, rapidly increases with decreasing temperature, whereas $\Delta l/l$ along the $b$ axis, that is $\Delta b/b$, continues to decrease. As far as the crystal keeps a hexagonal symmetry, $\Delta a/a$ and $\Delta b/b$ should coincide with each other even though it thermally expands or contracts. As clearly seen in Fig. 1 $\Delta a/a$ starts to deviate from $\Delta b/b$ at a higher temperature than 20 K ($> T_Q$). This behavior appears to correspond closely to that of the transverse modulus $C_{66}$ which starts to soften gradually below $\sim 20$ K. The precursor is possibly ascribed to the fluctuation of the quadrupolar ordering. Figure 2 shows the difference $\Delta a/a - \Delta b/b$, which is proportional to the expected spontaneous strain $e_{xx} - e_{yy}$. Thus, we succeeded in direct confirmation of the macroscopic distortion due to the ferroquadrupolar ordering in UCu$_2$Sn. The magnitude of the strain evaluated at 5 K is $4.5 \times 10^{-5}$. This is the reason why we could not detect any corresponding strain by the powder X-ray diffraction with a resolution of $10^{-3}$. However, the present value is one order of magnitude smaller than the value of $5.6 \times 10^{-4}$ which was estimated from the parameter values fitted to the elastic modulus observed. When a hexagonal system undergoes a structural transition, a 60 degrees ferroelastic-type domain is expected to appear in the ordered state. In the present case of UCu$_2$Sn, we believe to have observed the average of the spontaneous strain over those domains. The calculated value of $5.6 \times 10^{-4}$ should be regarded as the maximum value of the macroscopic strain expected for a single-domain sample.

The ground state doublet $\Gamma_5$ has a degeneracy of quadrupoles $O_{xy}$ and $O_{z}^2$. One of these order parameters should emerge below $T_Q$ and therefore the corresponding strain of $e_{xy}$ or $e_{xx} - e_{yy}$ is expected to appear spontaneously. In the present experiment, only the $e_{xx} - e_{yy}$ component was detected. This result strongly

![Figure 1](image1.png)

**FIG. 1:** Temperature dependence of thermal expansion $\Delta l/l$ along the $a$ and $b$ axes are shown by open circles and solid triangles, respectively.

![Figure 2](image2.png)

**FIG. 2:** Temperature dependence of $\Delta a/a - \Delta b/b$. 

Note: The text contains a few technical terms and equations, which might require specific knowledge to fully understand. The diagrams illustrate the thermal expansion behavior as a function of temperature, showing the distinct trends for different axes. The discussion delves into the experimental setup, the observed phenomena, and their implications.
suggests that the order parameter is $O_2^0$. However, here, we should just notice a possibility that the present experimental setup may disregard the $e_{xy}$ strain technically even though it emerges. As depicted in Fig. 3(a), a change in the sample length along the $x$ direction, consequently the strain $e_{xx} - e_{yy}$, can be directly measured since we capacitively detect the change in spacing between the parallel-plate electrodes. In the case of the strain $e_{xy}$, the sample will rotate so as to fit the two surfaces of the sample onto the parallel plates as shown in Fig. 3(b). The change $\Delta d$ in the inter-plate spacing will be negligibly small because $\Delta d$ is proportional to $(1 - \frac{1}{2} e_{xy}^2 + \cdots)$.

Shown in Fig. 4 is the temperature dependence of thermal expansion $\Delta l/l$ along the $c$ axis. At high temperatures, $\Delta c/c$ decreases monotonically with decreasing temperature. It increases gradually below $\sim 20$ K and rapidly below $T_Q$. We have no convincing explanation for this increase in $\Delta c/c$, but a possible origin might be related to development of the secondary order parameter $O_2^0$ which couples to $2e_{zz} - e_{xx} - e_{yy}$. As we reported previously, the strain-quadrupole coupling coefficient between $2e_{zz} - e_{xx} - e_{yy}$ and $O_2^0$ is very large.

The thermal expansion coefficient $\alpha_i$ is related to $\delta l/l$ by the following equation:

$$\alpha_i = \frac{1}{\delta T} \frac{\delta l_i}{l_i},$$

where $\delta$ and the subscript $i$ denote an infinitesimal difference and each axis, respectively. Figure 5 shows the thermal expansion coefficients $\alpha$ as a function of temperature along the $a$, $b$ and $c$ axes. Here, we assumed that the background variation of the thermal expansion coefficient is given by $\alpha_{bg} = AT + BT^3$. The values used for the fitting parameters $A$ and $B$ are listed in Table I. From these data, we can estimate the pressure effects on the transition temperature $T_Q$, using the Ehrenfest rela-
where the volume expansion coefficient $\Delta \beta$ is assumed as
\[ \Delta \beta = \Delta \alpha_a + \Delta \alpha_b + \Delta \alpha_c. \]
$V_m$ is the molar volume and $\Delta C_p$ is the change in the isobaric specific heat at $T_Q$. We used the difference between $\alpha_{bg}$ and $\alpha_i$ for $\Delta \alpha_i$ at $T_Q$. The uniaxial pressure effects on the transition temperature $T_Q$ are estimated from this result. The values of $dT_Q/dP_i$ along the $a$, $b$ and $c$ axes are listed in Table II.

To our knowledge, this is the first report on the uniaxial pressure effects on the transition temperature $T_Q$. The uniaxial pressure effect on $T_Q$ is also estimated to be $dT_Q/dP = -6.0 \times 10^{-1}$ K/GPa. This value is quite consistent with the value $dT_Q/dP = -9.6 \times 10^{-1}$ K/GPa reported for polycrystalline UCu$_2$Sn by Kurisu et al. \cite{16}.

### IV. CONCLUSION

We measured the thermal expansion along the $a$, $b$ and $c$ axes of single-crystalline UCu$_2$Sn. The change in the thermal expansion below $T_Q$ clearly indicates the spontaneous emergence of the macroscopic strain $e_{xx} - e_{yy}$, which couples to the quadrupole $O_2^2$. As a result, it is completely proved that the transition in UCu$_2$Sn at $T_Q$ originates from the ferroquadrupolar ordering. The enhancement of $\Delta c/c$ below $T_Q$ might be regarded as due to the development of the secondary order parameter $O_2^2$. We also discussed the uniaxial pressure effect on $T_Q$, and succeeded in evaluating $dT_Q/dP_i$.

### V. ACKNOWLEDGMENTS

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\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
axis & $A$ (K$^{-2}$) & $B$ (K$^{-4}$) \\
\hline
$a, b$ & $3.21 \times 10^{-8}$ & $3.73 \times 10^{-11}$ \\
$c$ & $6.46 \times 10^{-8}$ & $4.75 \times 10^{-11}$ \\
\hline
\end{tabular}
\caption{Fitting parameters $A$ and $B$ for the background $\alpha_{bg}$ of thermal expansion coefficients.}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
 & $dT_Q/dP_a$ & $dT_Q/dP_b$ & $dT_Q/dP_c$ \\
\hline
$-4.02 \times 10^{-4}$ & $+2.65 \times 10^{-4}$ & $-4.60 \times 10^{-4}$ \\
\hline
\end{tabular}
\caption{Uniaxial pressure effects on the transition temperature $T_Q$. The values for $dT_Q/dP_i$ are listed in K/GPa.}
\end{table}