Spontaneous strain due to ferroquadrupolar ordering in UCu$_2$Sn

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The ternary uranium compound UCu$_2$Sn with a hexagonal ZrPt$_3$Al-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 $\Gamma_5$. 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 $\varepsilon_{xy}$ strain, which couples to the ground state doublet $\Gamma_5$. 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 has been intensively investigated in a number of 4$f$-electron compounds. In the case of 5$f$-electron systems, however, the multipolar ordering has been reported only in a few compounds, including NpO$_2$, UPd$_3$, URu$_2$Si$_2$, UNiSn, and UCu$_2$Sn. Previously, we pointed out that UCu$_2$Sn and UNiSn undergo ferroquadrupolar ordering at low temperatures.

The compound UCu$_2$Sn has a hexagonal ZrPt$_3$Al-type structure (space group $P6_3/mmc$) 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—Sn, Cu, U, and Cu—where all U atoms occupy equivalent sites forming a triangle lattice. Takabatake et al. found that UCu$_2$Sn underwent a phase transition around 16 K. Afterwards, the transition was estimated to be a nonmagnetic one since Mössbauer and NMR spectroscopies inferred the absence of a hyperfine field at Sn and Cu sites and neutron diffraction detected no magnetic reflection. In our previous study on the specific heat and elastic moduli of UCu$_2$Sn, we determined the crystal electric field (CEF) parameters ($B^{(3)}_0 = 1.682 \times 10^3$ K, $B^{(3)}_6 = -6.100 \times 10^{-2}$ K, $B^{(5)}_0 = -1.720 \times 10^{-3}$ K, and $B^{(5)}_6 = 2.257 \times 10^{-1}$ K) and the CEF level scheme from the ground state non-Kramers doublet $\Gamma_5$ to the fifth excited state $\Gamma_3$, where $\Gamma_3$ is the irreducible representation for the $6/mmm$ point group. We also explained the reasons why the U ions formed the 5$f^2$ configuration with the total angular momentum $J = 4$ and the 5$f$ electrons were in the localized regime. The most prominent feature was that of the transverse modulus $C_{66}$, which exhibited the huge softening around $T_Q = 16$ K, which was evidence for the ferroquadrupolar ordering of the ground state $\Gamma_5$. The modulus $C_{66}$ is the linear response to $\varepsilon_{x'y'} = e_{xy}$ and $-e_{xy}$ strain in the hexagonal lattice. Taking into account 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 $g^Q_{xy}$, that is, ferroquadrupolar coupling in the ground state. To distinguish the quadrupolar ordering from the cooperative Jahn-Teller transition, we employed a nondimensional parameter $D = |g' C_0 g^Q N_0|$, 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 $g'$ predominates over the strain-quadrupole coupling $g$ in UCu$_2$Sn 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 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 $|e_{xy}| = N_0 k_B T \Gamma_3 (O_{xy}) / C_0$ with the parameters obtained from fitting the elastic modulus observed, and we found that the spontaneous strain might be as small as $5.6 \times 10^{-4}$. The value was smaller than the resolution of our x-ray diffraction ($= 1 \times 10^{-3}$). In the present work, we have carried out the thermal expansion experiments on a single-crystalline sample by a capacitance method.

II. EXPERIMENT

A single crystal of UCu$_2$Sn was grown by a Bridgman method. The details of sample preparation were described elsewhere. 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 $\Delta T$ 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. The plates have an area of $1.55 \times 10^{-2} \text{ mm}^2$. The value of $\frac{D_l}{l}/(40 \text{K})$ for each axis was defined as $\frac{\Delta l}{l(T)} - \frac{l(40 \text{K})}{l(40 \text{K})}$. The $a$ and $c$ axes are referred to the international tables (space group $P6_3/mmc$). 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 $\Delta l/l$ along the $a$ and $b$ axes both. At high temperatures, $\Delta l/l$ along both the $a$ and $b$ axes decreases 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 $\sim 20 \text{ K}$. 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° 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.

![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.](image1)

![FIG. 2. Temperature dependence of $\Delta a/a - \Delta b/b$.](image2)

![FIG. 3. (a) Schematic illustration of the experimental setup for the capacitance measurement. In this configuration, we can measure the change in the length along the $x$ direction. (b) Experimental setup for measuring $e_{xy}$ across $T_Q$.](image3)

![FIG. 4. Temperature dependence of thermal expansion $\Delta l/l$ along the $c$ axis.](image4)
expected for a single-domain sample.

The ground-state doublet $\Gamma_3$ has a degeneracy of quadrupoles $O_{xy}$ and $O_{zz}^2$. One of these order parameters should emerge below $T_Q$ and therefore the corresponding strain of $e_{xy}$ or $e_{zz}e_{yy}$ is expected to appear spontaneously. In the present experiment, only the $e_{xx}$ component was detected. This result strongly suggests that the order parameter is $O_{yy}^2$. 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 interplate spacing will be negligibly small because $\Delta d$ is proportional to $(1-(3/2)e_{xx}^2+\cdots)$.

Figure 4 shows the temperature dependence of thermal expansion $\Delta l/l$ along the $c$ axis, that is, $\Delta c/c$. 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 $2e_{zz}e_{yy}e_{yy}$. 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 $\alpha_{bg} = A T + B T^3$. 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 relation

$$\frac{dT_Q}{dP} = \frac{\Delta \beta T_Q V_m}{\Delta C_p},$$

where the volume expansion coefficient $\Delta \beta$ is assumed as $\Delta \beta = \Delta \alpha_x + \Delta \alpha_y + \Delta \alpha_z$. $V_m$ 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 effect in UCu$_2$Sn. The hydrostatic 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. 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 emer-
gence 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 being due to the development of the secondary order parameter $O_2^0$. We also discussed the uniaxial pressure effect on $T_Q$, and succeeded in evaluating $dT_Q/dP_i$.

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