Spontaneous strain due to ferroquadrupolar ordering in UCu_2Sn

Isao Ishii, Haruhiro Higaki, Toshiro Takabatake, Hiroshi Goshima, Toshizo Fujita, and Takashi Suzuki*
Department of Quantum Matter, ADSM, Hiroshima University, Higashi-Hiroshima 739-8530, Japan

Kenichi Katoh
Department of Applied Physics, National Defense Academy, Yokosuka 239-8686, Japan

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The ternary uranium compound UCu_2Sn with a hexagonal $ZrPt_2Al$-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 nonKramers doublet Γ_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 e_{xx}-e_{yy} strain, which couples to the ground state doublet Γ_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 $4f$-electron compounds.[1] In the case of $5f$-electron systems, however, the multipolar ordering has been reported only in a few compounds, including NpO_2,[2] UPd_3,[3] URu_2Si_2,[4] UNiSn,[5] and UCu_2Sn.[6] Previously, we pointed out that UCu_2Sn and UNiSn undergo ferroquadrupolar ordering at low temperatures.

The compound UCu_2Sn has a hexagonal $ZrPt_2Al$-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_2Sn underwent a phase transition around 16 K.[7] Afterwards, the transition was estimated to be a nonmagnetic one since Mössbauer[8] and NMR[9] spectroscopies inferred the absence of a hyperfine field at Sn and Cu sites and neutron diffraction detected no magnetic reflection.[10] In our previous study on the specific heat and elastic moduli of UCu_2Sn,[6] we determined the crystal electric field (CEF) parameters ($B_2^0 = 1.682\times 10$ K, $B_4^0 = -6.100\times 10^{-2}$ K, $B_6^0 = -1.720\times 10^{-3}$ K, and $B_6^6 = 2.257\times 10^{-1}$ K) and the CEF level scheme from the ground state non-Kramers doublet Γ_5 to the fifth excited state Γ_3, where Γ_i is the irreducible representation for the $6/mmm$ point group. We also explained the reasons why the U ions formed the $5f^2$ configuration with the total angular momentum $J = 4$ and the $5f$ 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 Γ_5. The modulus C_{66} is the linear response to e_{Γ_5} ($= e_{xy}$ and $= e_{xx}$-e_{yy}) 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'_{Γ_5}, that is, ferroquadrupolar coupling in the ground state. To distinguish the quadrupolar ordering from the cooperative Jahn-Teller transition, we employed a nondimensional parameter $D \equiv |g' C_0 / g^2 N_0|$,[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' predominates over the strain-quadrupole coupling g in UCu_2Sn 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[6] 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 $|e_{xy}| = N_0 k_B g_{\Gamma_5} \langle O_{xy}\rangle / C_0$[12] with the parameters obtained from fitting the elastic modulus observed, and we found that the spontaneous strain might be as small as 5.6×10^{-4}. The value was smaller than the resolution of our x-ray diffraction ($\simeq 1\times 10^{-3}$). In the present work, we have carried out the thermal expansion experiments on a single-crystalline sample by a capacitance method.[13]

II. EXPERIMENT

A single crystal of UCu_2Sn was grown by a Bridgman method. The details of sample preparation were described elsewhere.[10] An impurity phase of UCuSn ($\sim 4\%$) was detected in our single-crystalline sample of UCu_2Sn by the electron probe microanalysis. The sample was shaped in a rectangular parallelepiped of $2.824\times 2.908\times 3.288\ \mathrm{mm}^3$. 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

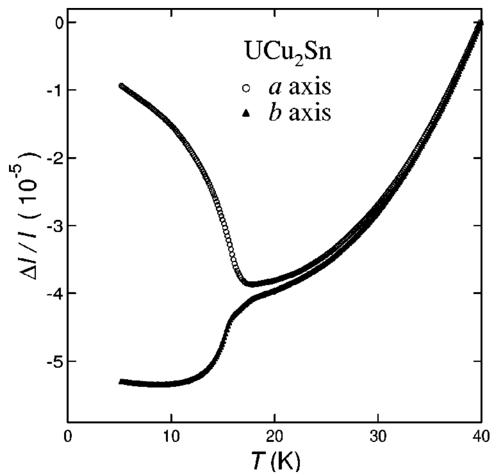

FIG. 1. Temperature dependence of thermal expansion $\Delta l/l$ along the *a* and *b* axes are shown by open circles and solid triangles, respectively.

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 $\simeq 1.55\times 10^2$ mm^2. The value of $\Delta l/l$ for each axis was defined as $[l(T)-l(40\mathrm{K})]/l(40\mathrm{K})$. The *a* and *c* axes are referred to the international tables (space group $P6_3/mmc$).[14] 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

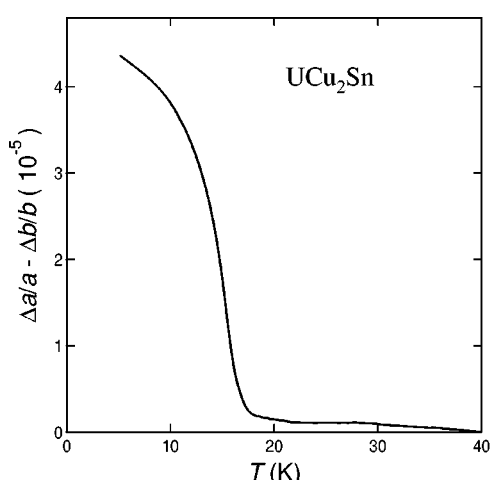

FIG. 2. Temperature dependence of $\Delta a/a - \Delta b/b$.

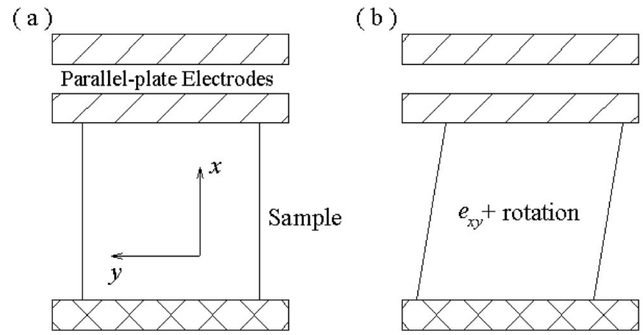

FIG. 3. (a) Schematic illustration of the experimental setup for the capacitance measurement. In this configuration, we can measure the change in the length along the *x* direction. (b) Experimental setup for measuring e_{xy} across T_Q.

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 ~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_2Sn. The magnitude of the strain evaluated at 5 K is 4.5×10^{-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 5.6×10^{-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_2Sn, we believe to have observed the average of the spontaneous strain over those domains. The calculated value of 5.6×10^{-4} should be regarded as the maximum value of the macroscopic strain ex-

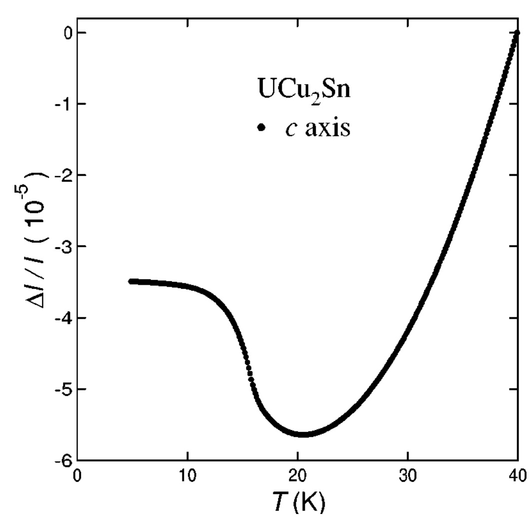

FIG. 4. Temperature dependence of thermal expansion $\Delta l/l$ along the *c* axis.

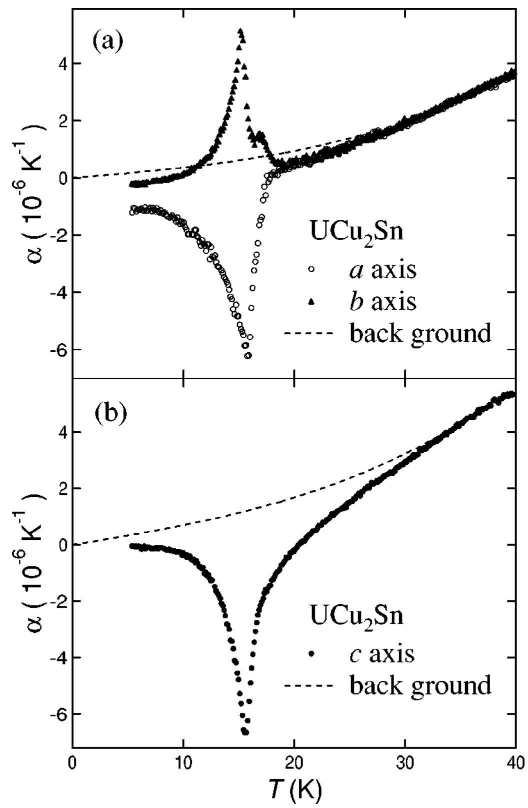

FIG. 5. Temperature dependence of the thermal expansion coefficient $\alpha(T)$. (a) Open circles denote α measured along the *a* axis and solid triangles along the *b* axis. The broken curve indicates the background α_{bg}. (b) Solid circles denotes α along the *c* axis and the broken curve indicates the background.

pected for a single-domain sample.

The ground-state doublet Γ_5 has a degeneracy of quadrupoles O_{xy} and O_2^2. 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 suggests that the order parameter is O_2^2. 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 Δd in the interplate spacing will be negligibly small because Δd

TABLE I. Fitting parameters *A* and *B* for the background α_{bg} of thermal expansion coefficients.

Axis	A (K^{-2})	B (K^{-4})
a, b	3.21×10^{-8}	3.73×10^{-11}
c	6.46×10^{-8}	4.75×10^{-11}

TABLE II. Uniaxial pressure effects on the transition temperature T_{Q}. The values for $\mathrm{d}T_{\mathrm{Q}}/\mathrm{d}P_i$ are listed in K/GPa.

$\mathrm{d}T_{\mathrm{Q}}/\mathrm{d}P_a$	$\mathrm{d}T_{\mathrm{Q}}/\mathrm{d}P_b$	$\mathrm{d}T_{\mathrm{Q}}/\mathrm{d}P_c$
-4.02×10^{-1}	$+2.65\times10^{-1}$	-4.60×10^{-1}

is proportional to $(1-(3/2)e_{xy}^2+\cdots)$.

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 ~ 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,[6] the strain-quadrupole coupling coefficient between $2e_{zz}$-e_{xx}-e_{yy} and O_2^0 is very large.

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

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

where δ and the subscript *i* denote an infinitesimal deference and each axis, respectively. Figure 5 shows the thermal expansion coefficients α 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 $\alpha_{\mathrm{bg}}=AT+BT^3$.[15] 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

$$\frac{\mathrm{d}T_{\mathrm{Q}}}{\mathrm{d}P}=\frac{\Delta\beta T_{\mathrm{Q}}V_{\mathrm{m}}}{\Delta C_{\mathrm{p}}},$$

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 ΔC_{p} is the change in the isobaric specific heat at T_{Q}. We used the difference between α_{bg} and α_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 $\mathrm{d}T_{\mathrm{Q}}/\mathrm{d}P_i$ 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 $\mathrm{UCu_2Sn}$. The hydrostatic pressure effect on T_{Q} is also estimated to be $\mathrm{d}T_{\mathrm{Q}}/\mathrm{d}P=-6.0\times10^{-1}$ K/GPa. This value is quite consistent with the value $\mathrm{d}T_{\mathrm{Q}}/\mathrm{d}P=-9.6\times10^{-1}$ K/GPa reported for polycrystalline $\mathrm{UCu_2Sn}$ by Kurisu *et al.*[16]

IV. CONCLUSION

We measured the thermal expansion along the *a*, *b*, and *c* axes of single-crystalline $\mathrm{UCu_2Sn}$. 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_2Sn 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 dTQ/dPi.

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*Electronic address: tsuzuki@hiroshima-u.ac.jp

[1] P. Morin and D. Schmitt, in *Ferromagnetic Materials*, Vol. 5, edited by K.H.J. Buschow and E.P. Wohlfarth (North-Holland, Amsterdam, 1990), p. 1.
[2] P. Santini and G. Amoretti, Phys. Rev. Lett. **85**, 2188 (2000).
[3] K.A. McEwen, U. Steigenberger, K.N. Clausen, J. Kulda, J.G. Park, and M.B. Walker, J. Magn. Magn. Mater. **177-181**, 37 (1998).
[4] P. Santini and G. Amoretti, Phys. Rev. Lett. **73**, 1027 (1994).
[5] T. Akazawa, T. Suzuki, H. Goshima, T. Tahara, T. Fujita, T. Takabatake, and H. Fujii, J. Phys. Soc. Jpn. **67**, 3256 (1998).
[6] T. Suzuki, I. Ishii, N. Okuda, K. Katoh, T. Takabatake, T. Fujita, and A. Tamaki, Phys. Rev. B **62**, 49 (2000).
[7] T. Takabatake, H. Iwasaki, H. Fujii, S. Ikeda, S. Nishigori, Y. Aoki, T. Suzuki, and T. Fujita, J. Phys. Soc. Jpn. **61**, 778 (1992).
[8] S. Wiese, E. Gamper, H. Winkelmann, B. Büchner, M.M. Abd-Elmeguid, H. Micklitz, and T. Takabatake, Physica B **230-232**, 95 (1997).
[9] K. Kojima, A. Harada, T. Takabatake, S. Ogura, and K. Hiraoka, Physica B **269**, 249 (1999).
[10] T. Takabatake, M. Shirase, K. Katoh, Y. Echizen, K. Sugiyama, and T. Osakabe, J. Magn. Magn. Mater. **177-181**, 53 (1998).
[11] P.M. Levy, P. Morin, and D. Schmitt, Phys. Rev. Lett. **42**, 1417 (1979).
[12] B. Lüthi, in *Dynamical Properties of Solids*, edited by G.K. Horton and A.A. Maradudin (North-Holland, Amsterdam, 1980).
[13] A. de Visser, Ph.D. thesis, Amsterdam University, 1986.
[14] *International Tables for Crystallography*, 2nd ed., edited by T. Hahn, Space-Group Symmetry Vol. A (Kluwer Academic, Dordrecht, 1989).
[15] T.H.K. Barron, J.G. Collons, and G.K. White, Adv. Phys. **29**, 609 (1980).
[16] M. Kurisu, T. Takabatake, H. Iwasaki, and H. Fujii, Physica B **206&207**, 505 (1995).