

Ultrasonic Investigation of Magnetic Ordering with Higher-Order Interactions in the Cage-Structured Compound $\text{U}_3\text{Pd}_{20}\text{Si}_6$

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Abstract. The elastic properties of localized $5f$ -electron system $\text{U}_3\text{Pd}_{20}\text{Si}_6$ were studied by means of ultrasonic measurements under magnetic fields. We have measured elastic constants C_{11} , $(C_{11}-C_{12})/2$, C_{44} and $C_{L110} = C_B + (C_{11}-C_{12})/6 + C_{44}$ in order to check a possible contribution of electric quadrupoles on the magnetically ordered phases of this compound for $\Gamma_1 \oplus \Gamma_3$, Γ_3 , Γ_5 and $\Gamma_1 \oplus \Gamma_3 \oplus \Gamma_5$ symmetries elastic response, respectively. We discovered that an elastic anomaly, which is accompanied by ultrasonic attenuation maximum of Γ_5 -symmetry mode, at around $T^* \sim 16$ K in zero magnetic field and shifts to lower temperatures with increasing magnetic fields. Since the T^* seems to be continuously connected to the lower boundary of a 'spin-flop' region in the magnetic field-temperature phase diagram of $\text{U}_3\text{Pd}_{20}\text{Si}_6$, we conclude that a fluctuation of the spin-system of the $8c$ -site ion exists even just below T_N and couples to elastic wave via magneto-elastic coupling with Γ_5 -symmetry quadrupoles of U's $5f$ electron or local charge distributions of the guest U ion.

1. Introduction

Many exotic physical phenomena have been found in several cage structural compounds, which have recently become a subject of special interest: such as unconventional superconductivity, multipolar order, and local anharmonic oscillation of the guest atom, so called rattling, which could be originated from its characteristic high-symmetric and over-sized cage structure. The cage-structured intermetallic compound $R_3\text{Pd}_{20}X_6$ (R = rare-earth and U, X = Si, Ge) has the Cr_{23}C_6 -type cubic structure, where R ion is located at two different crystallographic sites surrounded by atomic cage consisting of Pd and X atoms. In $\text{U}_3\text{Pd}_{20}\text{Si}_6$, each U-site shows magnetic phase transitions: antiferromagnetic (AFM) ordering at $T_N = 19$ K for $8c$ site (T_d symmetry) and ferromagnetic one at $T_C \sim 2$ K for $4a$ site (O_h symmetry) [1, 2]. The estimated effective moment of $3.4\mu_B/\text{U}$ indicates a relatively localized $5f$ -electron state. Such well localized- $5f$ state in Uranium compound is quite unique. The crystalline electric field ground state of both sites is Γ_5 triplet, which is consistent with magnetic entropy of $R\ln 3$ released at each transitions estimated from the specific heat and the detailed level scheme has been confirmed by inelastic neutron scattering [3]. Since the product space of Γ_5 triplets in cubic symmetry contains all of the five electric quadruples as active multipole, a possible quadrupole's



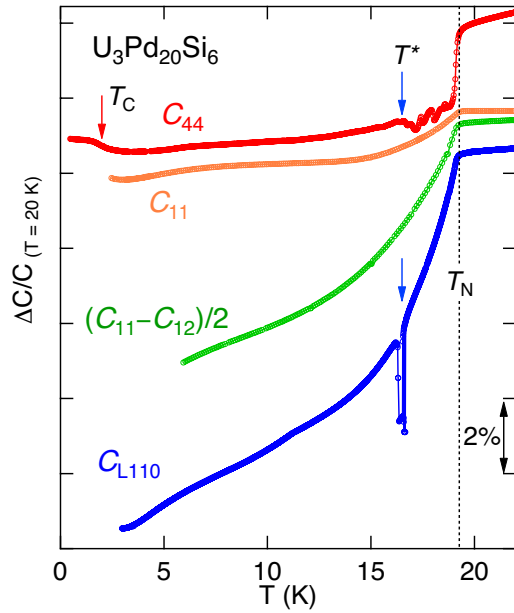


Figure 1. Relative change of elastic constants, longitudinal C_{11} and C_{L110} , transverse C_{44} and $(C_{11}-C_{12})/2$, as a function of temperatures, which were measured by constant phase (CP) method (see text). Vertical dotted line at $T_N = 19$ K represents AFM transition on $8c$ -site. Lower arrows show elastic anomalies regarding to $T^* \sim 16.5$ K and $T_C \sim 2$ K.

contribution on the ordered phase is highly expected. Indeed, the magnetic structure of the $8c$ -site's AFM ordering changes to a 'spin-flopped' collinear structure in the magnetic fields at low temperatures, which is considered to be a result of higher-order exchange and/or quadrupolar interactions of U ions [4]. Ultrasonic measurement provides information of such quadrupole responses. Our previous work of elastic constants of the present compound in zero magnetic field shows softening of the transverse C_{44} mode with Γ_5 symmetry in paramagnetic state above T_N , which is consistent with the Γ_5 triplet CEF ground state model. On the other hand, the relatively large softening just below T_N had suggested a presence of Γ_5 quadrupole's contribution also in the ordered state. In the present work, we noticed, however, that the previously reported large softening of 30% in C_{44} mode below T_N [5] becomes intrinsically smaller ($\sim 2\%$) after using a mirror polished single crystal. We also found that the magnetic field makes further suppression of the small softening (such as will be mentioned later). These facts suggest that ultrasound is strongly scattered by magnetic domain and/or fluctuation of the AFM moment, which results in smaller signal-to-noise ratio and, thus, makes the ultrasonic velocity measurement difficult for the temperature region just below T_N [5]. The motivation of the present work is to investigate the phase diagram in more detail by using higher frequency ultrasound, *i.e.*, the sound wave having higher directionality for small specimen, to see the possible quadrupole's response, in particular for intermediate temperature and magnetic-field region of the $8c$ -AFM phase which has not been investigated in detail.

2. Experimental Details

A single crystal of $U_3Pd_{20}Si_6$ has been grown at Japan Atomic Energy Agency by using Czochralski method. The surfaces of the sample, with the length of ~ 1.4 mm for $[001]$ -axis, were carefully polished by polishing paper #5000. Ultrasonic velocity measurements were performed by using conventional phase comparative methods. The ultrasonic velocity change has doubly been checked by using two different methods, constant-phase (CP) method, so called 'constant- k ' method, and constant frequency (CF) method, so called 'orthogonal phase' method. The elastic constants C_{11} , $(C_{11}-C_{12})/2$, C_{44} and $C_{L110} = C_B + (C_{11}-C_{12})/6 + C_{44}$ are measured by different ultrasonic modes: $k \parallel u \parallel [001]$, $k \parallel [110]$, $u \parallel [\bar{1}\bar{1}0]$ for $(C_{11}-C_{12})/2$, $k \parallel [001]$, $u \perp [001]$ for C_{44} and $k \parallel u \parallel [110]$ for C_{L110} in the present work, which couple to the strain fields with

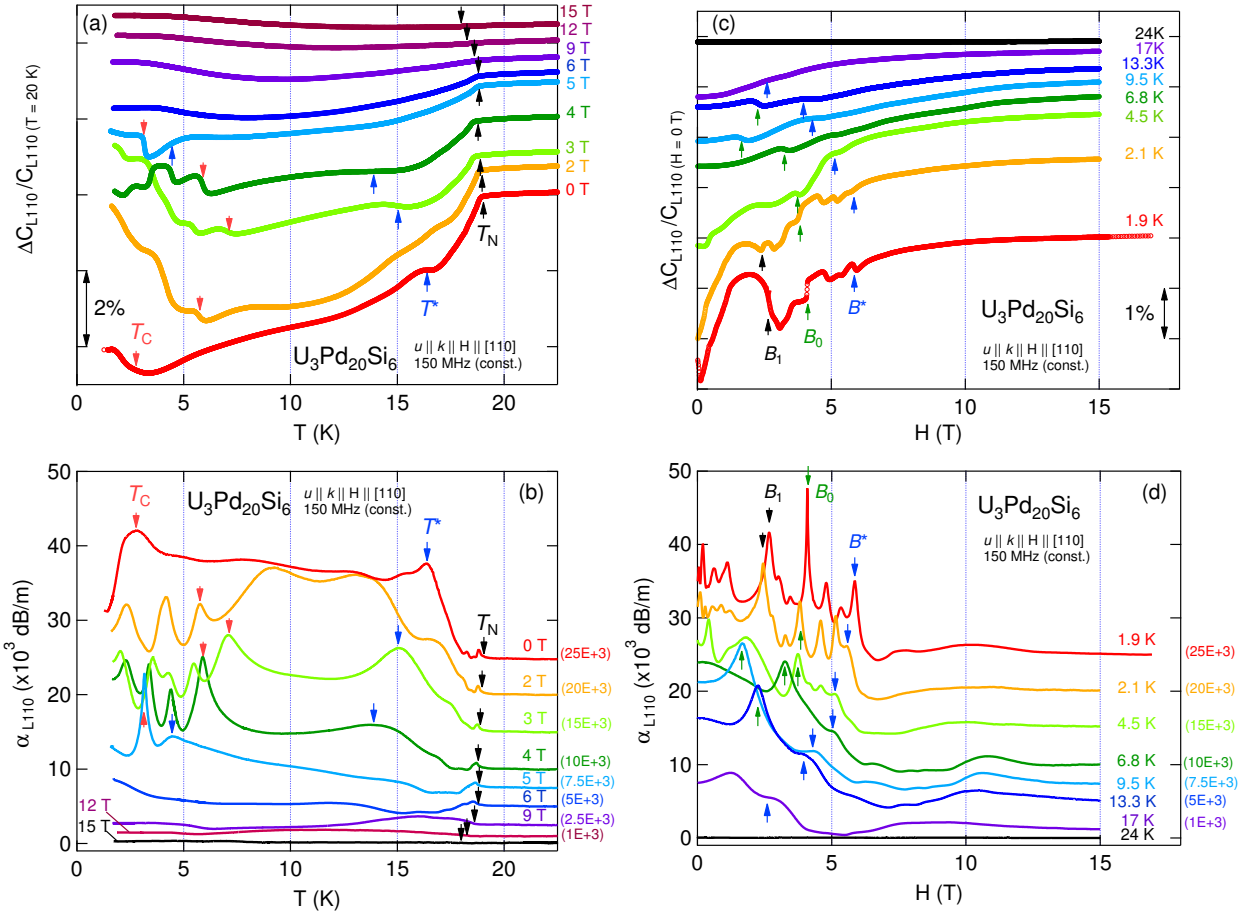


Figure 2. (a) Relative change of the elastic constant $\Delta C_{L110}/C_{L110}$ and (b) Ultrasonic attenuation coefficient α_{L110} vs temperatures at several fixed magnetic fields. (c) Relative change of the elastic constant $\Delta C_{L110}/C_{L110}$ and (d) Ultrasonic attenuation coefficient vs magnetic field at several fixed temperatures. The data is observed by using constant frequency (~ 150 MHz) method and displayed with offset for clarity. Arrows indicate the identified elastic anomalies (see text).

$\Gamma_1 \oplus \Gamma_3$, Γ_3 , Γ_5 and $\Gamma_1 \oplus \Gamma_3 \oplus \Gamma_5$ symmetry, respectively.

3. Results and Discussions

Figure 1 shows comparing of four different elastic constants as a function of temperature below 22 K, which were measured by CP method. All the elastic constant decrease below T_N . The transverse C_{44} mode exhibits sudden softening of $\sim 2\%$ below T_N which is rather smaller than the huge softening of $\sim 30\%$ in our previous report. Such overestimation in the previous work would be caused by untraceable ultrasonic echo due to strong ultrasonic attenuation just below T_N . In the present measurements, the ultrasonic echo is improved owing to that the sample surfaces were polished well and higher ultrasonic frequencies were used, thus, we conclude that the present value of 2% is more reliable result for C_{44} . The newly found elastic anomaly at T^* can be seen in the C_{44} and longitudinal C_{L110} modes, both of which contains Γ_5 components. Since the other modes C_{11} and $(C_{11}-C_{12})/2$ do not show any elastic anomaly around T^* , we can, therefore, simply conclude that the T^* anomaly is related to Γ_5 -symmetry breaking lattice

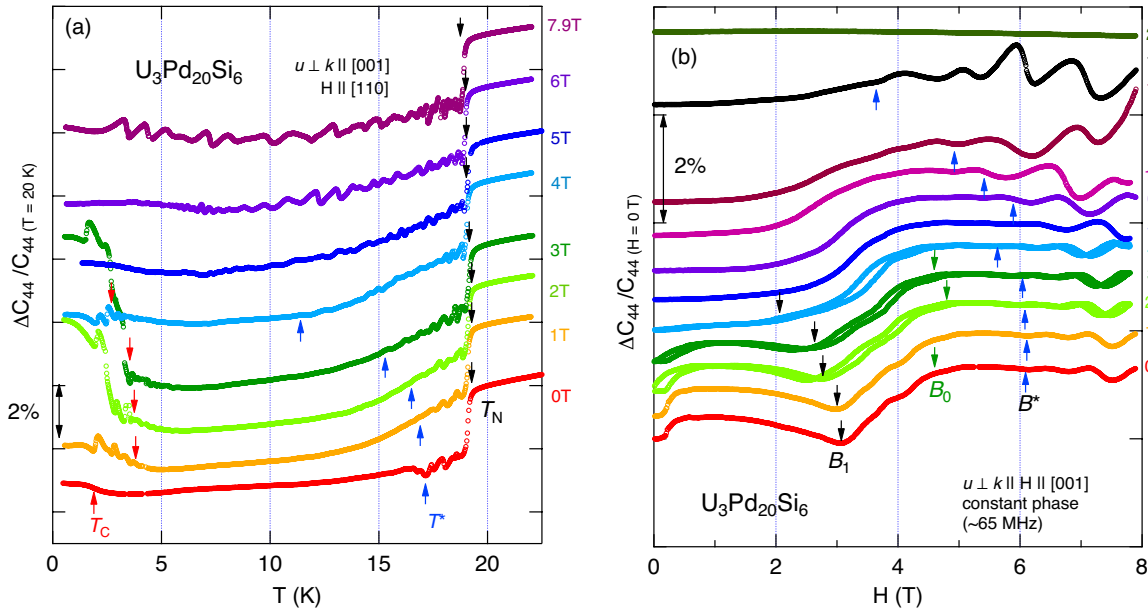


Figure 3. (a) Relative change of the elastic constant $\Delta C_{44}/C_{44}$ vs temperature at several fixed magnetic fields along the [110] axis of a $\text{U}_3\text{Pd}_{20}\text{Si}_6$ single crystal, for $0 \leq H \leq 7.9$ T by using constant phase method (~ 100 MHz). (b) Relative change of the elastic constant $\Delta C_{44}/C_{44}$ vs magnetic fields along the [001] axis of $\text{U}_3\text{Pd}_{20}\text{Si}_6$ at several fixed temperatures by using constant phase method (~ 65 MHz). The data are shifted vertically with spaced offset for clarity. Arrows indicate the observed elastic anomalies (see text)

instability. In addition, C_{44} shows unusual oscillation of the elastic constant observed by CP method below T_N , which will be discussed later. A criterion for determination of the T^* in C_{44} is the temperature where the oscillation subsides below T_N . The elastic anomaly of C_{L110} using CP method shows sudden dip at T^* , which may include experimental error due to CP method, since the T^* is observed as a broad kink in elastic constant and as an ultrasonic attenuation peak by using CF method (as shown in Fig. 2(a) and (b)).

Figures 2(a) and 2(c) show elastic constant C_{L110} as a function of temperature; Fig. 2(b) and 2(d) show ultrasonic attenuation coefficient α_{L110} as a function of magnetic field, both were measured by CF method. The elastic constant data is displayed as a relative change from 20 K and shifted vertically with spaced offset for clarity. The ultrasonic attenuation data is also shifted with the values represented next to the data. When applying the magnetic field, the softening below T_N and ultrasonic attenuation in the 8c-AFM phase gradually decrease and the T^* anomaly seems to be broaden but still clearly be observed as ultrasonic attenuation peak. Below 6 T at low-temperature region, several elastic anomalies, accompanied by ultrasonic attenuation peaks, are found. These anomalies below 7.5 K will be related to the phase III where 4a-site magnetic moments will order ferromagnetically and coexist with 8c-AFM [4]. In the magnetic field sweep at 1.9 K as shown in Figs. 2(c) and 2(d), the largest elastic anomaly with attenuation peak (indicated as B_1) is found inside of the phase III, which is consistent with the similar elastic anomaly found in C_{44} mode (as shown later) implying a presence of internal structures in the 4a-FM phase. The newly found anomaly T^* is also found in the magnetic field sweep, as a small elastic anomaly with attenuation peak or plateau in highest magnetic field indicated as B^* in Fig. 2(c) and 2(d). B_0 is determined as an another sharp attenuation peak below B^* . In the magnetic field sweep at 17 K, we can see a gradual upturn toward higher magnetic fields, which indicates that the magnetic field makes further suppression of the small

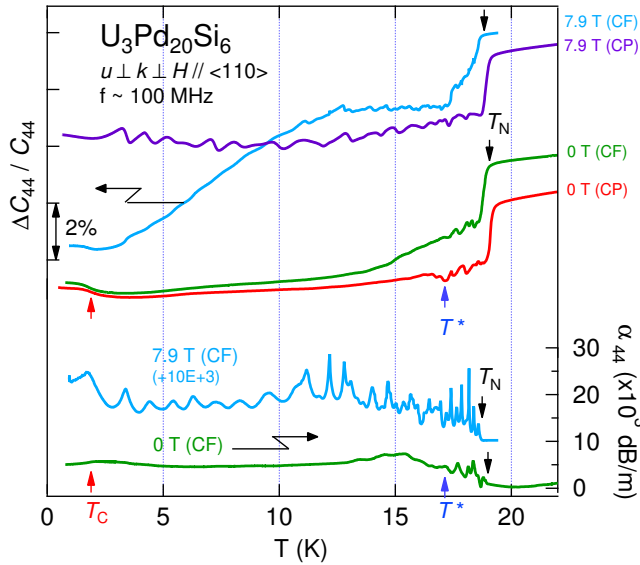


Figure 4. Comparison of relative change of elastic constant C_{44} observed by CP and CF methods (~ 100 MHz), as a function of temperatures below 22 K at 0 T and 7.9 T. In the lower part of the panel, ultrasonic attenuation coefficient, which is observed simultaneously by using CF method are shown as same color as the elastic constant data.

softening in temperature sweep below T_N .

Figures 3(a) and 3(b) show a Γ_5 -pure mode C_{44} obtained by CP method. In the magnetic field dependence (Fig. 3(b)), a hysteresis is found above B_1 , where we defined the high-magnetic field end of hysteresis region as B_0 which is consistent of the elastic anomaly found in C_{L110} with CF method (Figs. 2(c) and 2(d)). It is noted that unusual oscillation of the ultrasonic velocity is observed in the region between T_N and T^* . In 7.9 T, the oscillation can be found throughout the region below T_N . In Fig. 4, we compare the data observed by the constant phase (CP) method and constant frequency (CF) method for $H = 0$ T and 7.9 T. When we use the CF method, the oscillation in the ultrasonic velocity below T_N is not clearly observed, but such oscillation appears in the simultaneously obtained ultrasonic attenuation (right axis), instead. The data observed by CF method in 7.9 T shows additional softening below ~ 13 K while the data observed by CP method levels off at ~ 13 K with oscillation. In principle, both data of CP and CF methods must be the same, however the difference between CP and CF method could be caused by an instability of the sound propagation where the ultrasonic attenuation increases above 10×10^3 dB/m³. We are convinced that the CF method is better than the CP method for tracking such a strong scattered ultrasonic signals. Here, the CP method observes the ultrasonic velocity change as a change of ultrasonic frequency; therefore, we also suspect an intrinsic frequency-dependent elastic response in this region, which remain to be checked in future.

Since the anomalous oscillation of the ultrasonic velocity and attenuation in C_{44} mode are reproducible phenomena, and also found in the magnetic field sweep above B^* (as seen in Fig. 3(b)), these oscillations are not caused by magnetic-domain fluctuation. These oscillations also reminiscence a magneto-elastic wave due to spin-wave or acoustical Faraday effect in antiferromagnet [6]. These magneto-elastic wave had, however, been found in the ultrasonic measurements with \sim GHz time scale. The slower fluctuation time scale of \sim MHz of the present system is not comparable. On the other hand, the oscillation found in the temperature sweep is difficult to comprehend. Here, the possibility of multi- Q structures of the AF moments for 8c-site can be ruled out because of the lattice symmetry [7]. The microscopic origin of the frequency dependent oscillation in Γ_5 -mode and its relation to the possible higher order interaction, which cause the spin-flop of the AF moments with tilted structure in the magnetic fields, are still unknown and open questions. One assumption for such MHz-order dynamical-

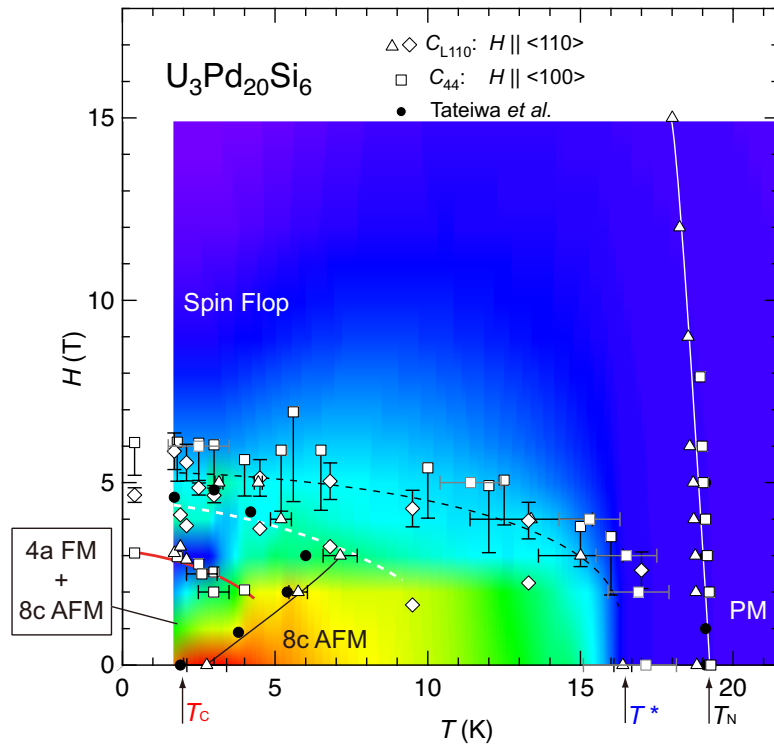


Figure 5. Magnetic field-temperature (H - T) phase diagram for $\text{U}_3\text{Pd}_{20}\text{Si}_6$, compiled from features in the elastic constants C_{L110} and C_{44} together with ultrasonic attenuation coefficients α_{L110} and α_{44} . The solid and dotted lines are guides to the eye; the white-solid line and black-solid line represents the boundary of T_N and T_C , while the black-dotted line, the white-dotted line and the red-solid line correspond to each bundle of the anomaly related to B^* , B_0 and B_1 , respectively. The colour background of the phase diagram represents the contour plot of magnitude of the normalized elastic constant C_{L110} for $H \parallel [110]$, where blue region indicate larger and red region indicate smaller in magnitude of elastic constant.

phenomena of the ultrasonic-velocity modulation is that spin-fluctuation of 8c-AF moment with the energy dissipation via interaction between 8c-site and 4a-site. The magnetic entropy and magnetization in the present compound indicate that the 4a-site will still be paramagnetic, *i.e.*, Γ_5 -symmetry electric quadrupoles are still active, even in the 8c-AFM phase. Such inter-site interaction will cause a damping of AF fluctuation amplitude and reduce the time-scale of the spin and quadrupole fluctuations. Another assumption is the local charge fluctuation of the 4a-site's U-ion. For example, the $\text{La}_3\text{Pd}_{20}\text{Ge}_6$ and other rare-earth systems exhibit a characteristic ultrasonic dispersion due to rattling in the C_{44} mode of same ultrasonic frequency range [8]. These facts imply that such anharmonic potential also exist in the present $\text{U}_3\text{Pd}_{20}\text{Si}_6$ and could results another energy dissipation via electron-phonon interaction. In addition, the relatively stronger hybridization between conduction electrons and 5f-electrons in U ion compare to the light lanthanides, there might be underlying a parity-mixing effect because the U 8c-site has no inversion symmetry.

Figure 5 represents a magnetic field-temperature (H - T) phase diagram for $\text{U}_3\text{Pd}_{20}\text{Si}_6$, which is revised by present ultrasonic measurements. On the contour plot in the background of the Fig. 5, we can clearly see there exists yellowish (light)-color region inside the 8c-AFM phase where the ultrasonic velocity of C_{L110} mode is relatively slower than the blue (dark)-color region. Slower ultrasonic velocity means smaller elastic constant indicating elastic softening region, where the

Table 1. Symmetry classification of magnetic-dipole and electric-quadrupole moments of cubic system with external magnetic fields $H \parallel [001]$ and $H \parallel [110]$.

| Magnetic Field Direction | Point Group | Symmetry | Dipole | Quadrupole | Elastic Constant | Coupled Ultrasonic Mode |
|--------------------------|-------------|------------------|-------------|-------------------|-------------------|--|
| $H \parallel [001]$ | C_{4v} | $\Gamma_1 (A_1)$ | J_z | O_2^0 | C_{11} | $k \parallel u \parallel [001]$ |
| | | $\Gamma_5 (E)$ | J_x, J_y | O_{zx}, O_{yz} | C_{44} | $k \parallel [001], u \perp [001]$ |
| $H \parallel [110]$ | C_{2v} | $\Gamma_1 (A_1)$ | $J_x + J_y$ | O_2^0, O_{xy} | C_{L110} | $k \parallel u \parallel [110]$ |
| | | | | | C_{66} | $k \parallel [100], u \parallel [010]$ |
| | | $\Gamma_3 (B_1)$ | J_z | $O_{yz} + O_{zx}$ | C_{L011} | $k \parallel u \parallel [011]$ |
| | | | | | C_{44} | $k \parallel [100], u \parallel [001]$ |
| | | $\Gamma_4 (B_2)$ | $J_x - J_y$ | O_2^2 | $C_{11} - C_{12}$ | $k \parallel [110], u \parallel [\bar{1}\bar{1}0]$ |

system has lattice instability.

In the intermediate region of 8c-AFM phase between 2 T and 6 T, we found a new boundary or crossover line, which is represented as a dark dashed line in Fig. 5. We define the T^* as the temperature, where the elastic anomaly is observed just below T_N . The anomaly shifts to low temperatures with increasing magnetic field and seems to continuously merge to the ‘spin-flop’ region. Thus, we predict that the spin-flop state or similar AF fluctuation due to collinear coupling weakly exists in the intermediate region between T_N and T^* and also the region just below T_N in the H - T phase diagram even in zero magnetic field. Further neutron scattering measurements in this intermediate temperature and magnetic-field region is needed to clarify the magnetic structure and its fluctuations between T_N and T^* .

Such coupling between spin flop and lattice can be understood as a result of magneto-elastic coupling from a simple symmetry aspect. Table 1 represents symmetry classification of dipoles and quadrupoles when the cubic point group symmetry of the U site is modified to C_{4v} and C_{2v} point groups depends on the external magnetic-field directions [9]. Since the spin-flop moment will be directed perpendicular to the magnetic field direction, we can see the spin-flop moment J_x, J_y for $H \parallel [001]$ and J_z for $H \parallel [110]$ definitely couple to the C_{44} mode via Γ_5 -symmetry quadrupole moments O_{yz} and O_{zx} .

In summary, we found that there is a region where the Γ_5 elastic response shows instability in the AFM phase of $U_3Pd_{20}Si_6$, which seems to divide the 8c-AFM phase into two regions and the high magnetic regions will merge to the spin-flop region. We conclude that the Γ_5 quadrupole moment of 5f-electrons or local charge distribution due to anharmonic potential in 4a-site cage is fluctuating in this region whose interaction couples to the tilted magnetic structure in low temperatures. In order to clarify these issues, frequency dependence of the ultrasonic measurements should firstly be achieved and further neutron scattering measurements or any other microscopic method below T_N in the magnetic field will also be needed.

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