Ultrasound Investigations of
Orbital Quadrupolar Ordering in UPd$_3$

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Abstract

For a high-quality single crystal of UPd$_3$ we present the relevant elastic constants and ultrasonic attenuation data. In addition to the magnetic phase transition at $T_2 = 4.4 \pm 0.1$K and the quadrupolar transition at $T_1 \sim 6.8$K, we find orbital ordering at $T_0 = 7.6 \pm 0.1$K concomitant with a symmetry change from hexagonal to orthorhombic. A striking feature is the splitting of the phase transition at $T_1$ into a second-order transition at $T_{+1} = 6.9 \pm 0.05$K and a first-order transition at $T_{-1} = 6.7 \pm 0.05$K. For the four phase transitions, the quadrupolar order parameters and the respective symmetry changes are specified.

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The actinide intermetallic nonheavy fermion system UPd$_3$ and the heavy fermion superconductor UPt$_3$ are hexagonal compounds with space group $P6_3/mmc$, exhibiting magnetic phase transitions at $T_2 = 4.4$K and $\sim 5$K, respectively. This finding is very surprising, because in both compounds the ordered magnetic moment is extremely small ($\mu \approx 10^{-2}\mu_B$).
Furthermore, the $5f$ electrons of $\text{UPt}_3$ are found to be predominantly itinerant, whereas $\text{UPd}_3$ belongs to the rather few metallic materials where well-localized $5f$ electrons and ionic long-range quadrupolar ordering at $T_1 = 6.8\text{K}$ has been identified. The possibility that quadrupolar order occurs at $T_1$ was first recognized in specific heat and thermal expansion measurements, and the strong quadrupole-quadrupole interaction between the $\text{U}$ ions was confirmed for the first time in sound velocity experiments, where also the relevant quadrupole components contributing to the magnetoelastic coupling were specified. The ultimate proof of the quadrupolar nature of the phase transition, however, was given in neutron scattering experiments, where the long-range lattice distortions which always accompany a quadrupolar phase transition were determined.

The main reason for the interest in the quadrupolar phase transition of $\text{UPd}_3$ is that the knowledge of the ordering components of the quadrupole tensor not only provides detailed information about the long-range ordering of the $5f^2$ electronic charge distribution of the uranium $\text{U}^{4+}$ ions (ground state $^3\text{H}_4$), but also of long-range spatial correlations of the orbital degrees of freedom. This is so, because the average values of the components $Q_{ij}$ of the electric quadrupole tensor $\mathbf{Q}$ are not only a measure of deviations of the localized $5f$ uranium electrons from a spherical charge distribution but, according to the identity $Q_{ij} \propto \{3(J_i J_j + J_j J_i)/2 + J(J+1)\}$, are also a measure of correlations between the components $J_i$ and $J_j$ of the total angular momentum $\mathbf{J}$. We mention that long-range quadrupolar (i.e., orbital) ordering is also of current interest in the context of the physics behind the colossal magnetoresistance in the manganates or the spin-Peierls and metal-insulator transitions in the vanadates.

In order to deduce from the lattice distortions the ordering quadrupole components $Q_{ij}$ (i.e., the order parameters), the complete strain tensor $\mathbf{\varepsilon}$ or, more strictly speaking, the symmetry adapted strains $\varepsilon_{\Gamma}$ must be known because the latter are proportional to the average value of the symmetry adapted components of the quadrupole tensor. In neutron diffraction experiments, however, the full strain tensor is difficult to deduce from the available Bragg peaks. This is one of the reasons why details concerning the various phase transitions...
and the proper order parameters in UPd$_3$ are still under discussion. Also, it is still an open question to what extent the inter-ion quadrupole-quadrupole interaction is responsible for the three reported phase transitions found at $T_2 = 4.4$K, $T_1 = 6.8$K and $T_0 = 7.8$K.

It is well known that ultrasound is well suited to answer these questions because the coupling of the acoustic strain $\varepsilon$ to the ionic quadrupole moment tensor $Q$ is, in general, large and the coefficients of the elastic stiffness tensor $C$ depend in a characteristic manner on the components of the so-called quadrupolar strain susceptibility $\chi^{(Q)}$. The latter is defined as $\delta Q = \chi^{(Q)} V$ and therefore is a measure of the response $\delta Q$ of the quadrupole moment tensor $Q$ to the strain-induced electric field gradient tensor $V$ at the uranium sites. The components $V_{ij}$ are related to the elastic strain tensor $\varepsilon$ via $V_{ij} = \sum S_{ijkl} \varepsilon_{kl}$, where the fourth-rank tensor $S$ is the so-called field gradient elastic strain tensor which may be determined in nuclear acoustic resonance experiments: this should not be confused with the elastic compliance tensor. The quadrupolar contribution $C^{(Q)}_\Gamma$ to a symmetry elastic constant $C_\Gamma$ is given by

$$C^{(Q)}_\Gamma = -N_V \frac{(S_{\Gamma(0)}^{(0)})^2 \cdot \chi^{(Q)}_{\Gamma}}{1 - g'_\Gamma \chi^{(Q)}_{\Gamma}}$$

where $N_V$ is the number density of quadrupoles, $g'_\Gamma$ the two ion quadrupole-quadrupole coupling constant and (depending on the irreducible representation $\Gamma$), $S_{\Gamma(0)}^{(0)}$ is a linear combination of the S-tensor components for $g'_\Gamma = 0$ (i.e., in the absence of the inter-ion quadrupole-quadrupole interaction). In terms of fluctuations [i.e., of the variance $(\Delta Q_{\Gamma})^2$] of the symmetry adapted quadrupole tensor components $Q_{\Gamma}$, the quadrupolar strain susceptibility $\chi^{(Q)}_{\Gamma}$ may be written in the thermostatic (zero-frequency) limit as $\chi^{(Q)}_{\Gamma} \propto (\Delta Q_{\Gamma})^2 / (k_B T)$, where, in general, five relevant quadrupole tensor components exist which, in the symmetry adapted form, we denote by $Q_{zz}, Q_x^2 - y^2 = Q_{xx} - Q_{yy}, Q_{xy}, Q_{yz}$, and $Q_{zx}$. If $Q_{\Gamma}$ is the order parameter, then a pronounced decrease of the related elastic constants $C_\Gamma$ (see Table I) should be observed at a second-order quadrupolar phase transition, because in that case, the fluctuations of $Q_{\Gamma}$ (and accordingly the strain susceptibility $\chi^{(Q)}_{\Gamma}$) should become large. Provided that at a quadrupolar phase transition the formation of domains or
its influence on the elastic behavior can be minimized such as to play only a minor role, then it becomes immediately evident that ultra-sound should be well suited to study long-range quadrupolar (i.e., orbital) ordering.

The efficiency of ultrasound is demonstrated in Figs. 1(a) and 2(a) for longitudinal acoustic waves propagating along the c axis of a rectangular single crystal of UPd$_3$ (with the linear dimensions 3.6 x 5.2 x 7.3 mm$^3$). As can be clearly seen, both the attenuation (phonon loss rate) and the sound velocity of the $C_{33}$ mode display three distinct phase transitions at $T_2 = 4.4 \pm 0.1$K, $T_1 \approx 6.8$K and $T_0 = 7.6 \pm 0.1$K, whereas the specific heat$^1$ and magnetic susceptibility$^2$ of samples of the same batch exhibit pronounced peaks only at $T_1$, and $T_1$ and $T_2$, respectively. Previous sound velocity$^3$ and neutron scattering experiments$^4$ revealed antiferroquadrupolar ordering at $T_1$ (Refs. 13 and 14) on the quasi-cubic uranium sites and it was thought that the concomitant structural transformation is from hexagonal to trigonal$^4$ or to orthorhombic$^5$ or monoclinic$^6$. At first sight, it is surprising that this transition dominates the specific heat but (compared to the magnitude of the ultrasound absorption peaks observed at $T_2$ and $T_0$) contributes only little to the phonon-loss rate. According to Table$^7$ and to Refs. 5 and 15, on the other hand, $\langle Q_{zz} \rangle$ is not the proper order parameter of a quadrupolar phase transition concomitant with a structural transformation from hexagonal to trigonal (monoclinic or orthorhombic). We therefore do not expect that the phonon-loss rate of the $C_{33}$ mode will be modified essentially in the vicinity of $T_1$ which is in agreement with our experimental findings (see Fig. 1). The absence of a huge absorption peak at $T_1$ (see Fig. 1) of both the $C_{33}$ and the $C_{44}$ mode further indicates that at $T_1$ the contribution of incoherent strains (originating from domains or domain walls) may be considered as negligibly small. This suggests that the ordered phase is the quadrupolar triple-$q$ state$^4$, because the triple-$q$ state avoids the formation of stochastically distributed domains. The development of the triple-$q$ state is associated with modulations of the electronic charge distribution. These modulations are a superposition of three plane waves with wave vectors $q_1$, $q_2$ and $q_3$, where the wave vectors $q_2$, and $q_3$ are obtained from $q_1$ by rotations of $\pm 2\pi/3$. The trigonal triple-$q$ phase (space group $P\overline{3}m1$) was discovered$^4$ in
neutron diffraction experiments and, within experimental uncertainty, the respective phase transition at $T_1$ was found to be continuous\(^\text{14}\). As we will see below, however, this is in contradiction to our findings.

We have mentioned already that the average value $\langle Q_{zz}\rangle$ cannot serve as a primary order parameter because it is already nonzero above $T_1$ (and $T_0$). The formation of the triple-$q$ phase may, nevertheless, modify the $C_{33}$ mode because the triple-$q$ state alters the $Q_{zz}$ moments of the cubic site ions. Surprisingly (see Fig. 2) the $C_{33}$ mode does not soften at $T_1$ upon cooling (as expected for a continuous phase transition), but shows a steplike increase which suggests that the transition at $T_1$ is most likely of first order. Even more surprising is the finding [see inset of Fig. 1(a)] that at around $T_1$ not one but two clearly distinguishable absorption peaks (and accordingly two phase transitions) appear at $T_{-1} = 6.7K$ and $T_{+1} = 6.9K$, where the stiffness coefficients $C_{33}$ and $C_{44}$ turn out to be hysteretic in the vicinity of $T_{-1}$ (see Fig. 3) but not at $T_{+1}$. In addition, [see Fig. 1(b)] we also have observed at $T_{-1}$ a pronounced hysteresis in the attenuation of the $C_{44}$ mode. The quadrupolar transition into the trigonal triple-$q$ state must therefore be of first order, whereas the transition at $T_{+1}$ is most likely of second order. We would like to emphasize that, to the best of our knowledge, for UPd$_3$ neither ultrasound absorption measurements nor the existence of the two neighboring phase transitions at $T_1$ have been previously reported. Compared to other experimental techniques, it is furthermore worthwhile to note (see Figs. 1 and 2) that at zero magnetic field the phase transition at $T_0 = 7.6K$ is most apparent in ultrasound.

So far, we have confined ourselves mainly to the $C_{33}$ mode which only reflects the temperature dependence of the secondary order parameter $\langle Q_{zz}\rangle$. For hexagonal symmetry (see Table I) a softening of the $C_{44}$ mode is attributed to an ordering of the quadrupole components $\langle Q_{yz}\rangle$ and/or $\langle Q_{zx}\rangle$, whereas the order parameters related to $C_{66} = (C_{11} - C_{12})/2$ (or to $C_{11}$ and $C_{22}$) are the degenerate quadrupoles $\langle Q_{xy}\rangle$ (or $\langle Q_{x^2-y^2}\rangle$). We now consider the temperature dependence of $C_{44}$ and $C_{66}$. As can be seen in Fig. 2, with decreasing temperature, $C_{44}$ exhibits a small dip at $T_{-1}$, followed by a steep decrease at the magnetic
transition temperature $T_2 = 4.4K$ which is accompanied by a very sharp peak (see Fig. 1) in the phonon loss rate. However, the most pronounced softening of the $C_{66}$ mode appears at $T_0 = 7.6K$, not at $T_1$ as reported for a sample of much lower crystal quality and size by other authors.\[10] The softening of the $C_{44}$ and $C_{66}$ modes, which starts already far above the transition temperatures $T_2$ and $T_0$, is very strong and it has been shown\[11] that below 150K the temperature dependence of the elastic constants is essentially due to the crystal-field splitting at the quasicubic uranium sites. We therefore conclude that not only at $T_1$, but also at $T_0$ and at the magnetic transition temperature $T_2$, the driving force of the respective phase transitions is of quadrupolar origin. Hence, the quadrupolar order parameter of the magnetic phase $(T < T_2)$ is most likely (see below) a linear combination\[13] of $Q_{y2}$ and $Q_{x2-y2}$, whilst at $T_0$ the relevant order parameters are the degenerate quadrupoles $Q_{xy}$ and $Q_{x2-y2}$. Here, degenerate means that the response of the respective quadrupoles is specified by the same strain susceptibility.

The degenerate order parameters $Q_{x2-y2}$ and $Q_{xy}$ which, according to Table I, will modify $C_{11}$, $C_{22}$ and $C_{66} = (C_{11} - C_{12})/2$, are associated with a transition from hexagonal to orthorhombic\[14] or to monoclinic\[15], whereas the order parameters $Q_{y2}$ and $Q_{x2}$ will change $C_{44}$ and $C_{55}$ and entail a transition from a hexagonal to either a monoclinic or triclinic phase\[15]. Here, the formation of a monoclinic or triclinic phase depends on whether or not both order parameters are present simultaneously. Since no anomaly is seen at $T_0 = 7.6K$ in the elastic modulus $C_{44}$, whereas the $C_{11}$ and $C_{22}$ modes (which are not shown here) and the $C_{66}$ mode soften significantly, it follows that at $T_0$ we pass with decreasing temperature from the hexagonal to an orthorhombic or monoclinic phase. When analyzing the phase transitions below $T_0$, we therefore have to take into account that for $T_+ < T < T_0$, the symmetry is orthorhombic or monoclinic but not hexagonal (which in the literature was taken for granted until recently). The monoclinic phase, however, may be excluded because in that case the only possible second-order transition at $T_+$ would be\[16] from a monoclinic to a triclinic phase, which is in contrast to our experimental findings (see Fig. 3), because such a transition should alter $C_{44}$ significantly. At $T_0$ the symmetry of UPd3, therefore, passes at
decreasing temperature from hexagonal to orthorhombic and the only possible-second order transition at $T_{+1}$ is from the orthorhombic to a monoclinic state. At $T_{+1}$ we therefore have to consider $\langle Q_{yz} \rangle, \langle Q_{zx} \rangle$, and $\langle Q_{xy} \rangle$ as possible order parameters, where $\langle Q_{yz} \rangle$ and $\langle Q_{zx} \rangle$ may be excluded because $C_{44}$ (see Fig. 3) and $C_{55}$ do not alter significantly at $T_{+1}$. Concerning $\langle Q_{xy} \rangle$, however, which should modify $C_{66}$, we cannot prove experimentally whether or not $\langle Q_{xy} \rangle$ becomes an order parameter at $T_{+1}$, because in the temperature range between 6.6K and 7.8K, the attenuation of the $C_{66}$ mode becomes too large. We note that in agreement with Ref. 15 and our experimental findings, the phase transition at $T_{-1}$ (i.e., from the monoclinic to the trigonal triple-$q$ state) is of first order. The softening of the $C_{44}$ mode at $T_2 = 4.4K$ further indicates that at decreasing temperature, UPd$_3$ transforms at $T_2$ from the trigonal triple-$q$ state into a monoclinic (magnetic) state, where the transition is expected to be of first order. Within experimental resolution, however, the $C_{44}$ mode does not show a signature of a first-order transition which indicates that at $T_2$ it is possibly not enough to consider the magnetoelastic coupling only. According to Ref. 15 the transition from the triple-$q$ into the monoclinic phase should be accompanied by the loss of the ternary axis and the order parameter should be a linear combination of $\langle Q_{yz} \rangle$ and $\langle Q_{x^2-y^2} \rangle$. It is therefore expected that both $C_{44}$ and $C_{66}$ will soften at $T_2$, which is confirmed by our experiments (see Fig. 2). In the immediate vicinity of $T_2$, however, the attenuation of the $C_{66}$ mode becomes too large to enable a more detailed analysis of this phase transition.

Based upon the crystal-field split ($J = 4$) multiplets determined by Buyers et al. 17 the temperature dependence of $C_{44}$ has been evaluated previously in Ref. 13 yielding the quadrupolar coupling constants $N_V(S_{44}^{(0)})^2/C_{44}^{(0)} = 0.6K$ and $g_{44}' = -6K$. Since the ordered magnetic moments in UPd$_3$ are so extremely small and the quadrupolar coupling constants are so large, the pronounced softening of the $C_{44}$ mode indicates that the quadrupole-quadrupole interaction is the most probable driving mechanism of the magnetic phase transition at $T_2$. Owing to the negative sign of the quadrupole coupling constant $g_{44}'$ we further expect antiferroquadrupolar ordering at $T_2$ and the formation of a very complex antiferromagnetic state, which is currently under investigation and will be the subject of a
forthcoming paper. Summarizing our results, we have shown that ultrasound is a powerful tool for investigating orbital ordering and that the large variety of interesting phase transitions in UPd$_3$ is of quadrupolar origin. We hope that our findings may also offer some new ideas in the attempt of a better understanding of the formation of the heavy fermion state and the antiferromagnetic transition in UPt$_3$.

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FIG. 1. Temperature dependence of the $\sim 20$MHz longitudinal (a) and transverse (b) attenuation coefficients of the $C_{33}$ and $C_{44}$ elastic modes.
FIG. 2. Temperature dependence of the elastic constants $C_{33}$, $C_{44}$, and $C_{66}$ at about 20MHz.
FIG. 3. Hysteretic behavior of the $C_{33}$ and $C_{44}$ elastic mode at about 22MHz.
TABLE I. Quadrupolar contribution $C_{\alpha\beta}^{(Q)}$ to the elastic constants in Voigt notation, the strain-induced quadrupole interaction Hamiltonian $H_Q$ and the relevant strain susceptibilities $\chi_{\Gamma}^{(Q)}$ for hexagonal crystal symmetry and different acoustic strain modes $\varepsilon_{ij}$. The indices x, y, and z refer to the a-, b-, and c-axis of the crystal.

| $\varepsilon_{ij}$ | $C_{\alpha\beta}^{(Q)}$ | $H_Q$ | $\chi_{\Gamma}$ |
|-------------------|--------------------------|-------|-----------------|
| $\varepsilon_{xx}$ | $C_{11}^{(Q)}$ | $-(S_{11} + S_{12})Q_{zz} + (S_{11} - S_{12})Q_{x^2-y^2}$ | $\chi_{zz}^{(Q)}$, $\chi_{x^2-y^2}^{(Q)}$ |
| $\varepsilon_{yy}$ | $C_{22}^{(Q)}$ | $-(S_{11} + S_{12})Q_{zz} - (S_{11} - S_{12})Q_{x^2-y^2}$ | $\chi_{zz}^{(Q)}$, $\chi_{x^2-y^2}^{(Q)}$ |
| $\varepsilon_{zz}$ | $C_{33}^{(Q)}$ | $S_{33}Q_{zz}\varepsilon_{zz}$ | $\chi_{zz}^{(Q)}$ |
| $\varepsilon_{yz}$ | $C_{44}^{(Q)}$ | $S_{44}Q_{yz}\varepsilon_{yz}$ | $\chi_{yz}^{(Q)}$ |
| $\varepsilon_{zx}$ | $C_{55}^{(Q)}$ | $S_{44}Q_{zx}\varepsilon_{zx}$ | $\chi_{zx}^{(Q)} = \chi_{yz}^{(Q)}$ |
| $\varepsilon_{xy}$ | $C_{66}^{(Q)}$ | $(S_{11} - S_{12})Q_{xy}\varepsilon_{xy}$ | $\chi_{xy}^{(Q)} = \chi_{x^2-y^2}^{(Q)}$ |