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Ultrasound investigations of orbital quadrupolar ordering in UPd_3

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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 $T_2=4.4\pm0.1$ K and the quadrupolar transition at $T_1 \sim 6.8$ K, we find orbital ordering at $T_0=7.6\pm0.1$ 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 $T_{+1}=6.9\pm0.05$ K and a first-order transition at $T_{-1}=6.7\pm0.05$ K. For the four phase transitions, the quadrupolar order parameters and the respective symmetry changes are specified. [S0163-1829(99)50736-4]

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 ~ 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 UPt_3 are found to be predominantly itinerant, whereas UPd_3 belongs to the rather few metallic materials where well-localized $5f$ electrons and ionic long-range quadrupolar ordering at $T_1=6.8$ K has been identified. The possibility that quadrupolar order occurs at T_1 was first recognized in specific heat[1] and thermal expansion[2] measurements, and the strong quadrupole-quadrupole interaction between the U ions was confirmed for the first time in sound velocity experiments,[3] 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,[4] where the long-range lattice distortions which always accompany[5] a quadrupolar phase transition were determined.

The main reason for the interest in the quadrupolar phase transition of 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 U^{4+} ions (ground state $^3H_4$), 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 $Q_{ij} \propto \{3(J_iJ_j+J_jJ_i)/2-\delta_{ij}J(J+1)\}$, 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[6] or the spin-Peierls and metal-insulator transitions[6] 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 $\boldsymbol{\varepsilon}$ or, more strictly speaking, the symmetry adapted strains ε_Γ must be known because the latter are proportional[5] 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.[7]

It is well known that ultrasound is well suited[8] to answer these questions because the coupling of the acoustic strain $\boldsymbol{\varepsilon}$ to the ionic quadrupole moment tensor $\mathbf{Q}$ is, in general, large and the coefficients of the elastic stiffness tensor $\mathbf{C}$ depend in a characteristic manner[5,8] (see Table I) on the components of the so-called quadrupolar strain susceptibility $\boldsymbol{\chi}^{(Q)}$. The latter is defined as $\delta\mathbf{Q}=\boldsymbol{\chi}^{(Q)}\mathbf{V}$ and therefore is a measure of the response $\delta\mathbf{Q}$ of the quadrupole moment tensor $\mathbf{Q}$ to the strain-induced electric field gradient tensor $\mathbf{V}$ at the uranium sites. The components $\mathbf{V}_{ij}$ are related to the elastic strain tensor $\boldsymbol{\varepsilon}$ via $\mathbf{V}_{ij}=\Sigma S_{ijkl}\varepsilon_{kl}$, where the fourth-rank tensor $\mathbf{S}$ is the so-called *field gradient elastic strain* tensor which may be determined[9] in nuclear acoustic resonance experiments: this should not be confused with the elastic compliance tensor. The quadrupolar contribution $C_\Gamma^{(Q)}$ to a symmetry elastic constant C_Γ is given by[8,10]

$$C_\Gamma^{(Q)} = -N_v \frac{(S_\Gamma^{(0)})^2 \chi_\Gamma^{(Q)}}{1-g_\Gamma' \chi_\Gamma^{(Q)}},$$

where N_v is the number density of quadrupoles, g_Γ' the two ion quadrupole-quadrupole coupling constant and (depending on the irreducible representation Γ), $S_\Gamma^{(0)}$ 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_Γ, the quadrupolar strain susceptibility $\chi_\Gamma^{(Q)}$ may be written in the

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 ε_{ij}. The indices *x*, *y*, and *z* refer to the *a*, *b*, and *c* axis of the crystal.

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

thermostatic (zero-frequency) limit as $\chi_\Gamma^{(Q)} \propto (\Delta Q_\Gamma)^2/(k_B T)$, 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_Γ is the order parameter, then a pronounced decrease of the related elastic constants C_Γ (see Table I) should be observed at a second-order quadrupolar phase transition, because in that case, the fluctuations of Q_Γ (and accordingly the strain susceptibility $\chi_\Gamma^{(Q)}$) 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 ultrasound 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 $3.6\times5.2\times7.3$ 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 $T_2=4.4\pm0.1$ K, $T_1\approx6.8$ K, and $T_0=7.6\pm0.1$ K, whereas the specific heat[11] and magnetic susceptibility[12] of samples of the same batch exhibit pronounced peaks only at T_1, and T_1 and T_2, respectively. Previous sound velocity[3,13] and neutron scattering experiments[14] revealed antiferroquadrupolar ordering at T_1 (Refs. 13 and 14) on the quasicubic uranium sites, and it was thought that the concomitant structural transformation is from hexagonal to trigonal[7,14] or to orthorhombic[3] or monoclinic.[3] 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 I 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,[14] 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 $\mathbf{q}_1$, $\mathbf{q}_2$, and $\mathbf{q}_3$, where the wave vectors $\mathbf{q}_2$ and $\mathbf{q}_3$ are obtained from $\mathbf{q}_1$ by rotations of $\pm 2\pi/3$. The trigonal triple-**q** phase (space group $P\bar{3}m1$) was discovered[14] in neutron diffraction experiments and, within experimental uncertainty, the respective phase transition at T_1 was found to be continuous.[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 be-

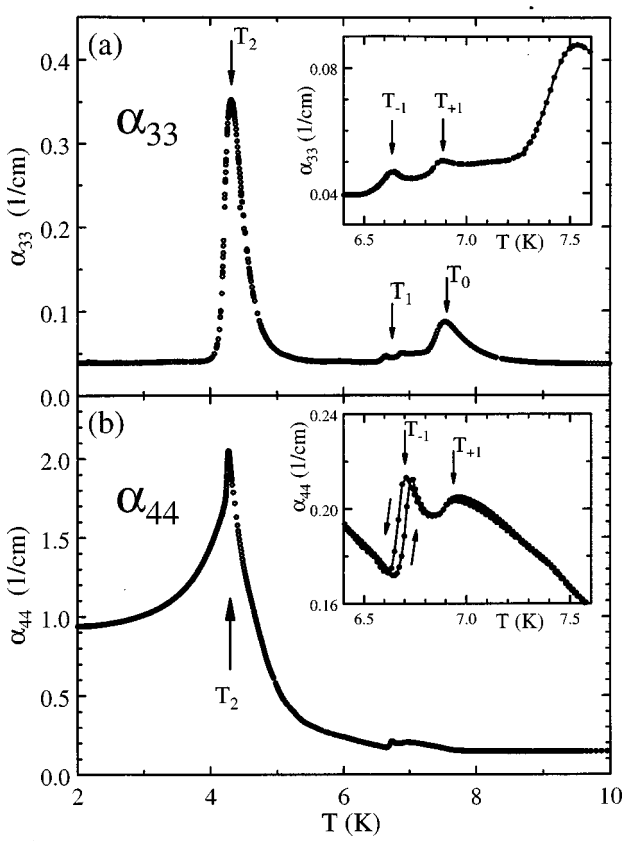

FIG. 1. Temperature dependence of the ~20 MHz longitudinal (a) and transverse (b) attenuation coefficients of the C_{33} and C_{44} elastic modes.

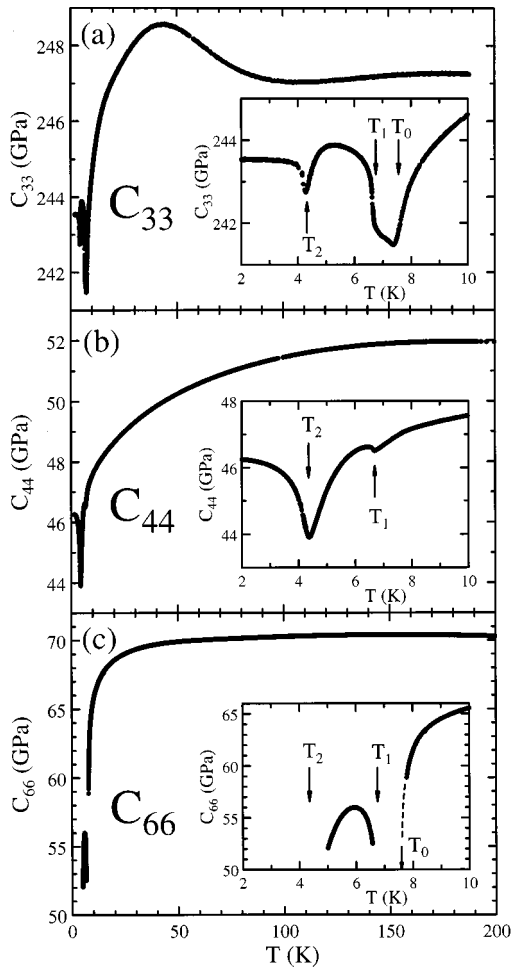

FIG. 2. Temperature dependence of the elastic constants C_{33}, C_{44}, and C_{66} at about 20 MHz.

cause the triple-**q** state alters[14] 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 $T_{-1}=6.7\,\mathrm{K}$ and $T_{+1}=6.9\,\mathrm{K}$, 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 $T_0=7.6\,\mathrm{K}$ 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

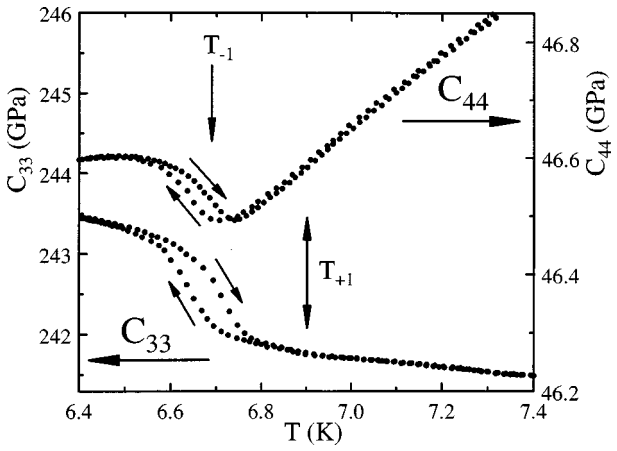

FIG. 3. Hysteretic behavior of the C_{33} and C_{44} elastic mode at about 22 MHz.

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 $T_2=4.4\,\mathrm{K}$ 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 $T_0=7.6\,\mathrm{K}$, not at T_1 as reported for a sample of much lower crystal quality and size by other authors.[3] 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[13] that below 150 K 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[15] of $\langle Q_{yz}\rangle$ and $\langle Q_{x^2-y^2}\rangle$, whilst at T_0 the relevant order parameters are the degenerate quadrupoles $\langle Q_{xy}\rangle$ and $\langle Q_{x^2-y^2}\rangle$. Here, *degenerate* means that the response of the respective quadrupoles is specified by the same strain susceptibility.

The degenerate order parameters $\langle Q_{x^2-y^2}\rangle$ and $\langle Q_{xy}\rangle$ 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[15,16] or to monoclinic,[16] whereas the order parameters $\langle Q_{yz}\rangle$ and $\langle Q_{zx}\rangle$ will change C_{44} and C_{55} and entail a transition from a hexagonal to either a monoclinic or triclinic phase.[15,16] 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 $T_0=7.6\,\mathrm{K}$ 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 $T_{+1}<T<T_0$, 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_{+1} would be[15] 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 UPd_3, therefore, passes at decreasing temperature from hexagonal to orthorhombic and the only possible second-order transition[15,16] at T_{+1} is from the orthorhombic to a monoclinic state. At T_{+1} we therefore have to consider[15,16] $\langle Q_{yz}\rangle$, $\langle Q_{zx}\rangle$, and $\langle Q_{xy}\rangle$ as possible order parameters, where $\langle Q_{yz}\rangle$ and $\langle Q_{zx}\rangle$ may be excluded[15,16] 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[15] 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 6.6 and 7.8 K, 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 $T_2=4.4$ K further indicates[15] 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[15] to be of first order. Within experimental resolution, however, the C_{44} mode doesn't 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 $N_v(S_{44}^{(0)})^2/C_{44}^{(0)}=0.6\,\mathrm{K}$ and $g'_{44}=-6\,\mathrm{K}$. Since the ordered magnetic moments in UPd_3 are so extremely small[4] 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[10,13] 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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