Determination of the Antiferroquadrupolar Order Parameters in UPd_3

H. C. Walker,[1] K. A. McEwen,[1,*] D. F. McMorrow,[1] S. B. Wilkins,[2] F. Wastin,[3] E. Colineau,[3] and D. Fort[4]

[1]*Department of Physics and Astronomy, University College London, Gower Street, London, WC1E 6BT, United Kingdom*
[2]*European Synchrotron Radiation Facility, Boîte Postale 200, F-38403, Grenoble Cedex, France*
[3]*European Commission, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, Karlsruhe, D-76125 Germany*
[4]*Department of Metallurgy, University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom*

(Received 15 March 2006; published 27 September 2006)

By combining accurate heat capacity and x-ray resonant scattering results we have resolved the long standing question regarding the nature of the quadrupolar ordered phases in UPd_3. The order parameter of the highest temperature quadrupolar phase has been uniquely determined to be antiphase Q_{zx} in contrast to the previous conjecture of $Q_{x^2-y^2}$. The azimuthal dependence of the x-ray scattering intensity from the quadrupolar superlattice reflections indicates that the lower temperature phases are described by a superposition of order parameters. The heat capacity features associated with each of the phase transitions characterize their order, which imposes restrictions on the matrix elements of the quadrupolar operators.

DOI: 10.1103/PhysRevLett.97.137203 PACS numbers: 75.25.+z, 75.10.−b, 75.40.Cx, 78.70.Ck

In the past couple of decades there has been considerable interest in the orbital ordering of d and f electron systems [1–11]. The highly degenerate f-electron shells in actinide and rare earth systems provide a wealth of local degrees of freedom: dipolar (magnetic), quadrupolar, octupolar, etc., In localized f-electron systems these degrees of freedom become potential order parameters, which can lead to interesting and complex phase diagrams. While, historically, the order associated with magnetic dipole moments has been studied extensively, more recently the importance of electric quadrupoles in magnetic materials has been recognized [12]. In classical electrodynamics the multipole expansion suggests that the interaction between higher order multipoles is seemingly much weaker than between dipoles. However, the interaction between multipoles is quantum mechanical in origin, and dipolar and quadrupolar interactions may be equally strong. More recently, quadrupolar order has been associated with new and interesting behavior, such as the novel heavy Fermion state in $PrFe_4P_{12}$ [6], and the exotic superconductivity in $PrOs_4Sb_{12}$, which may be mediated by quadrupolar fluctuations [7].

UPd_3 is a very interesting system, being a rare example of a localized uranium intermetallic compound, as well as belonging to the small class of metallic materials which exhibit long-range quadrupolar order. Despite intensive experimental investigation over the past 25 years an understanding of the series of four phase transitions below 8 K, and the exact nature of the quadrupolar ordering in UPd_3 has proved highly challenging. For the first time we are now able to distinguish which order parameter is associated with the highest temperature quadrupolar phase between $T = 7.8$ and 6.9 K. This has been achieved using the unique properties of x-ray resonant scattering (XRS), which may be visualized as a process in which an incident photon promotes a core electron to an excited intermediate state that then decays back to the initial state, emitting a scattered photon. XRS reveals information about the ordering of the ground state of multipoles associated with this intermediate state, since at resonance the scattering length becomes a tensor [13,14] whose elements are directly related to the multipole moments. Quadrupolar order describes the periodicity of charge distribution asphericities and additional superlattice reflections are observed in the case of antiferroquadrupolar (AFQ) ordering. Characterization of the dependence of such reflections on photon energy and polarization, and azimuthal angle (rotation around the scattering vector) allows details of the multipolar structure to be deduced by comparison with calculations based on tensors for the different order parameters [8–10].

UPd_3 crystallizes in the double-hexagonal close-packed (dhcp) structure (lattice parameters $a = 5.73$ Å, $c = 9.66$ Å), with uranium ions sitting at sites with locally hexagonal and quasicubic symmetry (space group $P6_3/mmc$). Four transitions at $T_0 = 7.8$ K, $T_{+1} = 6.9$ K, $T_{-1} = 6.7$ K, and $T_2 = 4.4$ K have been revealed by a combination of microscopic, e.g., neutron [15–18] and x-ray [11] scattering, and macroscopic measurements: ultrasound [19], heat capacity [20,21], magnetic susceptibility [21,22], thermal expansion, and magnetostriction [23]. The quadrupolar phase transitions are very sensitive to doping Np for U [24], and Pt for Pd [23]. Neutron [16–18] and x-ray [11] scattering studies indicate that the phase transition at T_0 is to an AFQ structure associated with periodic lattice distortions and a doubling of the double-hexagonal unit cell leading to superlattice reflections at $\mathbf{Q} = (2h + 1, 0, l)$ in the orthorhombic notation, which will be used hereafter. Polarized neutron diffraction (PND) measurements [18] suggested that the phase between T_0 and T_{+1} was $Q_{x^2-y^2}$, and the earlier x-ray experiments [11] were consistent with this hypothesis. However, due to limitations on cryostat technology, it was not possible to perform x-ray azimuthal scans at that time in the appropriate temperature regimes. Recently, a new crystal field model [25] with a doublet ground state on the quasicubic sites, as

opposed to the earlier singlet ground state model of Buyers *et al.* [15], provided a qualitative understanding of the succession of quadrupolar phase transitions with suggestions for the possible order parameters. It also presents a framework for understanding whether the transitions are first or second order. In this Letter, we present x-ray resonant scattering data which shows unequivocally that below T_0 the AFQ structure is described by the Q_{zx}, rather than $Q_{x^2-y^2}$, order parameter.

Previous heat capacity experiments were made before the T_{+1} and T_{-1} transitions had been identified, and so we have undertaken new measurements to distinguish the two transitions. The heat capacity of polycrystalline samples of 51.33 mg UPd_3 and 16.79 mg $ThPd_3$, used as a phonon blank, was measured from $T = 2$–300 K using a PPMS-9 Quantum Design calorimeter in the Actinide UserLab at the Institute for Transuranium Elements. Contributions to the heat capacity from the sample holder and grease were measured separately and then subtracted from the total signal.

Heat capacity results reveal a lambda anomaly below T_{-1}, which is clearly first order, while there are no large entropy changes at the other transitions, see Fig. 1. This affects the matrix elements for the order parameters. Using the three-level model developed by McEwen *et al.* [25], the matrices representing the quadrupolar operators can be written as

$$\hat{Q}_{x^2-y^2} = \begin{pmatrix} 0 & A & A \\ A & 0 & B \\ A & B & 0 \end{pmatrix} \quad \hat{Q}_{zx} = \begin{pmatrix} 0 & A' & A' \\ A' & 0 & B' \\ A' & B' & 0 \end{pmatrix}$$

$$\hat{Q}_{xy} = \begin{pmatrix} 0 & -Ai & Ai \\ Ai & 0 & -Bi \\ -Ai & Bi & 0 \end{pmatrix} \quad \hat{Q}_{yz} = \begin{pmatrix} 0 & A'i & -A'i \\ -A'i & 0 & B'i \\ A'i & -B'i & 0 \end{pmatrix}, \tag{1}$$

where the $A^{(\prime)}$ terms mix the singlet with the doublet states, and the $B^{(\prime)}$ terms split the doublet. From Landau theory the operators' symmetries mean that there should be at least two first-order transitions, while the data in Fig. 1(b) indicates that there is only one strongly first-order transition at T_{-1}. Since the $B^{(\prime)}$ term splits the ground doublet, leading to entropy changes at the transition, either B or B' must be $\simeq 0$, to make $\hat{Q} = -\hat{Q}$ for either $\hat{Q}_{x^2-y^2}$ or $\hat{Q}_{zx}$, such that there can be just one strongly first-order transition.

For the XRS experiment a single crystal of UPd_3 was grown, at the University of Birmingham, using the Czochralski method with starting materials of 99.9% pure U and 99.99% pure Pd. The experiment was performed on the ID20 beam line at the European Synchrotron Radiation Facility. Resonant scattering studies can be carried out at the L and M edges of uranium compounds, but since we wish to probe the f electrons, we used the M_{IV} edge, $E = 3.726$ keV, at which dipolar transitions connect the core $3d_{3/2}$ states to the $5f$ states. The electric dipole transitions, $E1$, dominate the resonant scattering cross section.

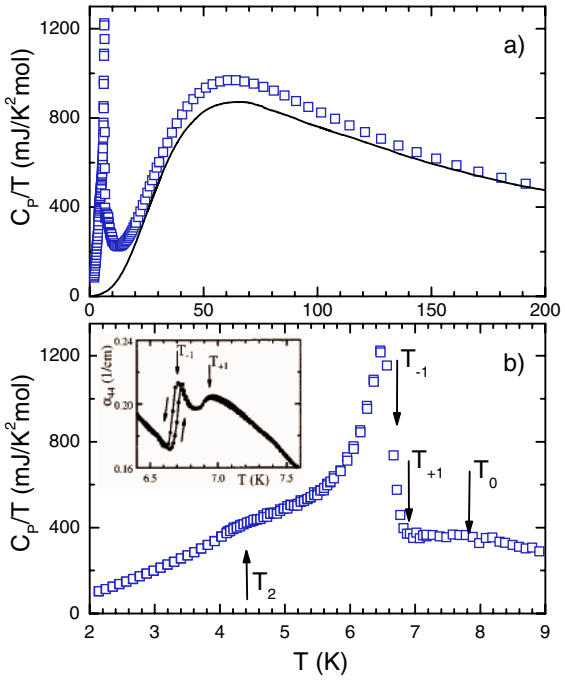

FIG. 1 (color online). (a) Heat capacity of UPd_3 and $ThPd_3$ (open blue squares and a black line, respectively), up to 200 K at which point the phonons are the dominant contribution to the heat capacity. (b) UPd_3 heat capacity in the region of the four transitions. The lambda anomaly clearly shows that the first-order transition is associated with T_{-1}, rather than T_{+1}. The inset shows ultrasonics data [19] from which the T_{-1} and T_{+1} transitions were first identified, with hysteresis in α_{44} at T_{-1}.

At $E = 3.726$ keV only a small region of reciprocal space is accessible. Therefore our crystal was cut with a reciprocal space (207) face such that both the (1, 0, 3) and (1, 0, 4) superlattice peaks could easily be measured over a wide range of Ψ. The 417 mg sample was polished with 0.25 μm diamond paste and mounted in an azimuth displex cryostat, allowing us to operate the diffractometer in the vertical plane, in which the incident x rays are σ-polarized: see Fig. 2 for a schematic of the experimental setup. This makes azimuthal rotation possible, unlike in the previous horizontal geometry experiment [11]. Polarization analysis was performed by mounting an Au (111) analyzer crystal. Data was normalized against the monitor.

The azimuthal dependence of the scattering intensity at the (1, 0, 3) reflection at $T = 7.1$ K, i.e., within the first quadrupolar phase, is shown in Fig. 3. The azimuth angle Ψ is defined relative to the reference vector $[0\bar{1}0]$. At each azimuthal angle, rocking curves were taken and the intensities of the $\sigma\sigma'$ and $\sigma\pi'$ polarization channels determined by fitting a Lorentzian squared line shape minimizing chi squared.

The azimuthal dependence of the allowed order parameters was calculated by summing the second rank tensors T_n

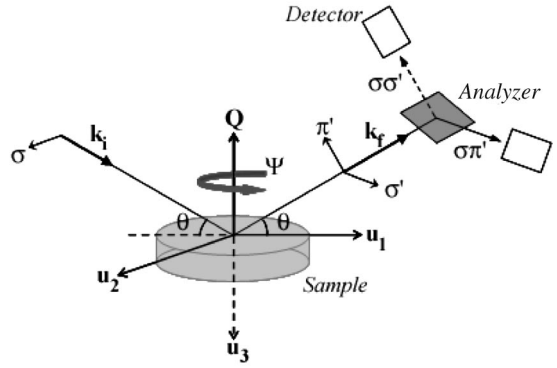

FIG. 2. A schematic of the setup for measuring the azimuthal dependence of the scattering intensity of a superlattice reflection at $\mathbf{Q}$. σ-polarized x rays incident at an angle θ on to the sample are scattered by a vector $\mathbf{Q}$. The scattered x rays are separated into the rotated, π', and unrotated, σ', channels by a polarization analyzer before detection. The sample stage is rotated to give an azimuthal angle Ψ about the scattering vector. The unit vectors $\mathbf{u}_i$ define the reference frame.

of the individual uranium quadrupoles to construct the resonant scattering length of the unit cell [11]

$$f = \sum_n T_n \exp(i\mathbf{Q} \cdot \mathbf{r}). \tag{2}$$

The scattering amplitude is then given by

$$A = \boldsymbol{\epsilon}' \cdot f \cdot \boldsymbol{\epsilon}, \tag{3}$$

where the incident ($\boldsymbol{\epsilon}$) and scattered ($\boldsymbol{\epsilon}'$) polarizations are transformed into the coordinate system of Blume and Gibbs [26] following the method of Wilkins *et al.* [9].

Figure 3 shows that the $(1, 0, 3)$ data is in excellent agreement with the above calculation for the azimuthal dependence of Q_{zx} antiferroquadrupolar order. In the $\sigma\pi'$ channel, note the asymmetry about $\Psi = 0°$ in both the data and Q_{zx} calculation, and that the maxima are not at

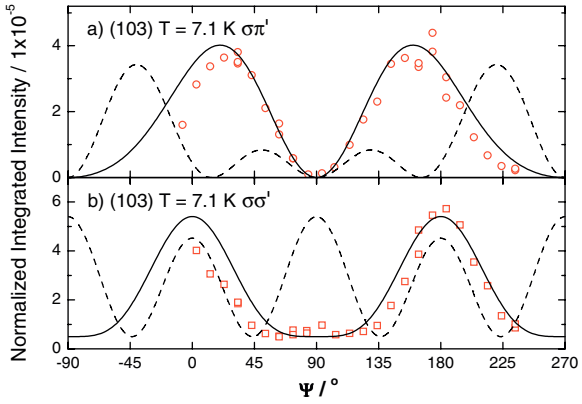

FIG. 3 (color online). The azimuthal dependence of (a) the $\sigma\pi'$ and (b) the $\sigma\sigma'$ scattering intensities of the $(1, 0, 3)$ peak in UPd_3 at the U M_{IV} edge, at $T = 7.1$ K. Comparison is made with calculations for the Q_{zx} (solid line) and the $Q_{x^2-y^2}$ (dashed line) order parameters.

$\Psi = 0°, 180°$. In the $\sigma\sigma'$ channel, the data and calculation show a broad minimum at 90° with symmetry about $\Psi = 0°$. Since our sample was cut with a (207) reciprocal lattice face, the scattering vector $\mathbf{Q} = (1, 0, 3)$ is not collinear with the face normal ($\mathbf{n}$). The σ' polarization vector is perpendicular to both $\mathbf{n}$ and $\mathbf{Q}$ so the noncollinear nature is not observed, resulting in the symmetry about $\Psi = 0°$ seen in $\sigma\sigma'$ azimuthal measurements. However, the π' polarization vector lies in the plane of $\mathbf{n}$ and $\mathbf{Q}$, and the noncollinearity leads to an asymmetry in the azimuthal variation in intensity. Calculations of the Ψ dependence of the scattering intensity for the $Q_{x^2-y^2}$, Q_{xy} and Q_{yz} order parameters do not agree with the data, as they show either the wrong periodicity, symmetry, or maxima and minima positions, and hence these order parameters can be ruled out. Q_{zx} provides a natural explanation for the macroscopic distortion to the orthorhombic cell [23] due to the splitting of the $x - y$ symmetry; see Fig. 4. Combining the knowledge that the transition at $T_0 = 7.8$ K is to a Q_{zx} AFQ ordering of the $5f^2$ electrons, with the heat capacity evidence that this transition is either second order or very weakly first order requires $B' \simeq 0$. Although the discussion in [25] assumed the order parameter was $Q_{x^2-y^2}$, with $B \simeq 0$, this model is equally valid for Q_{zx} as the operator matrices have the same symmetry; see Eq. (1).

In order to investigate the change in quadrupolar order in the different phases of UPd_3 seen in various measurements and the temperature dependence of the XRS [11], azimuthal measurements were made about both $\mathbf{Q} = (1, 0, 3)$ and $(1, 0, 4)$ at $T = 5.2$ K to study the third quadrupolar phase, see Fig. 5. These measurements were made in the $\sigma\pi'$ channel only, since there is considerable charge scattering interference in the $\sigma\sigma'$ channel, From the first-order

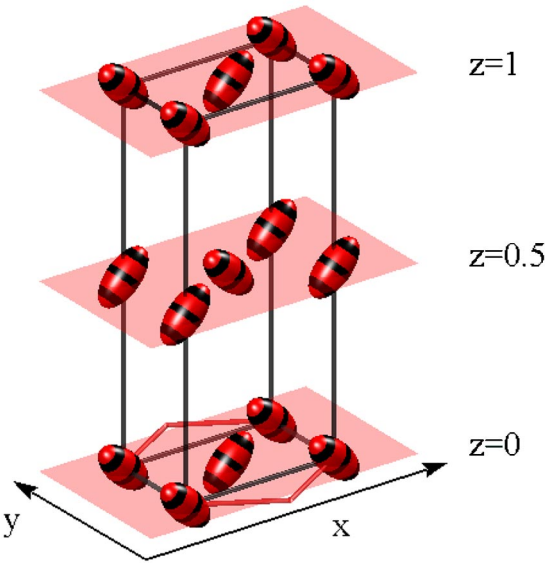

FIG. 4 (color online). The Q_{zx} AFQ structure with antiphase stacking along the z axis in UPd_3 at $T_{+1} < T < T_0$ in an orthorhombic unit cell. The U $5f$ quadrupoles on the quasicubic sites are represented schematically by ellipsoids.

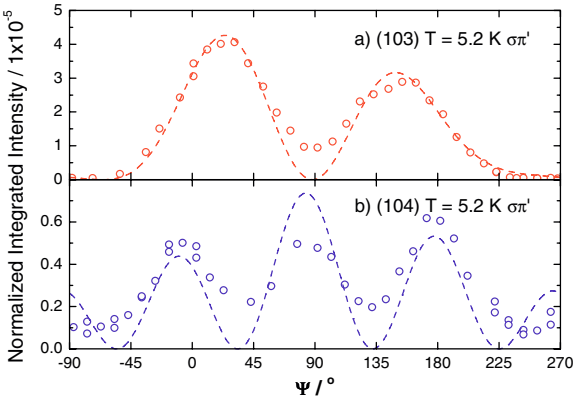

FIG. 5 (color online). The azimuthal dependence of the $\sigma\pi'$ scattered intensity from (a) the $(1, 0, 3)$ and (b) the $(1, 0, 4)$ superlattice peaks, in UPd_3 at the U M_{IV} edge, at $T = 5.2$ K. Dashed lines show least squares fits to the data as described in the text.

lambda peak in the heat capacity at T_{-1}, we expect to find evidence of an admixture of $Q_{x^2-y^2}$ in this phase. It is very difficult to stabilize the cryostat reliably between 6.7 and 6.9 K for extended periods and so we have concentrated on measuring azimuthal scans in the third quadrupolar phase. However, the heat capacity data indicates that at T_{+1}, $\Delta S \sim 0$, which would be consistent with the evolution of Q_{yz} order.

The azimuthal dependence of scattering from the $(1, 0, 3)$ peak reflects the part of the AFQ structure which varies in antiphase along the c axis, while that for the $(1, 0, 4)$ peak reflects that which is uniform along the c axis (in-phase stacking). Clearly the azimuthal dependence of the $\mathbf{Q} = (1, 0, 3)$ scattering at 5.2 K is more complicated than in the higher temperature Q_{zx} phase. A least squares fit to the data, varying the contributions from the allowed quadrupolar moments, indicates that Q_{zx} still predominates in the order parameter, but that Q_{xy} and $Q_{x^2-y^2}$ are also present. The fit in Fig. 5(a) is derived from an anomalous scattering tensor in which Q_{zx}, Q_{xy} and $Q_{x^2-y^2}$ are present in the ratio 77:10:13. The $(1, 0, 4)$ reflection, which is observed below T_{+1}, indicates the existence of in-phase (along the c axis) components to the order parameter, as well as the antiphase components deduced from the $(1, 0, 3)$ reflection. The fit to our data in Fig. 5(b), which reproduces the periodicity of the $(1, 0, 4)$ data, indicates that the most significant components are Q_{xy} and Q_{yz} in the ratio 2:1.

In conclusion, our new heat capacity measurements reveal only one strong first-order transition at $T = T_{-1}$, while $\Delta S \simeq 0$ at both T_{+1} and T_0. These observations constrain the quadrupolar operator matrix elements within our model [25]. Our azimuthal XRS experiments have unambiguously identified the order parameter for the first antiferroquadrupolar phase, $T_{+1} < T < T_0$, in UPd_3 as Q_{zx}. This may be reconciled with the PND $Q_{x^2-y^2}$ result, since those measurements were necessarily made in a magnetic field. Calculations show that the wave functions and energies of the crystal field states in our model [25] are significantly modified in fields of a few Tesla. We will examine with XRS the field behavior of the different quadrupolar phases in future experiments. Our results have provided further valuable insight into the nature of the other quadrupolar phases, indicating a surprisingly complex sequence of order parameters leading to a rotation of the charge densities.

We thank the European Community-Access to Research Infrastructures action of the Improving Human Potential Programme (IHP), Contract No. HPRI-CT-2001-00118. H. C. W. thanks EPSRC, and D. F. M. thanks the Royal Society for financial support. The authors thank L. Paolasini, C. Detlefs, and P. Deen for useful discussions and their assistance.

*Electronic address: k.mcewen@ucl.ac.uk

[1] Y. Murakami *et al.*, Phys. Rev. Lett. **80**, 1932 (1998).
[2] Y. Murakami *et al.*, Phys. Rev. Lett. **81**, 582 (1998).
[3] S. B. Wilkins *et al.*, Phys. Rev. Lett. **91**, 167205 (2003).
[4] K. J. Thomas *et al.*, Phys. Rev. Lett. **92**, 237204 (2004).
[5] R. Shiina, H. Shiba, and P. Thalmeier, J. Phys. Soc. Japan **66**, 1741 (1997).
[6] Y. Aoki *et al.*, Phys. Rev. B **65**, 064446 (2002).
[7] K. Izawa *et al.*, Phys. Rev. Lett. **90**, 117001 (2003).
[8] J. A. Paixão *et al.*, Phys. Rev. Lett. **89**, 187202 (2002).
[9] S. B. Wilkins *et al.*, Phys. Rev. B **70**, 214402 (2004).
[10] T. Matsumura *et al.*, Phys. Rev. B **65**, 094420 (2002).
[11] D. F. McMorrow *et al.*, Phys. Rev. Lett. **87**, 057201 (2001).
[12] P. Morin and D. Schmitt, *Ferromagnetic Materials* (North-Holland, Amsterdam, 1990), Vol. 5, p. 1.
[13] V. E. Dmitrienko, Acta Crystallogr. Sect. A **39**, 29 (1983).
[14] V. E. Dmitrienko, Acta Cryst. A **40**, 89 (1984).
[15] W. J. L. Buyers *et al.*, Physica (Amsterdam) **102B+C**, 291 (1980).
[16] U. Steigenberger *et al.*, J. Magn. Magn. Mater. **108**, 163 (1992).
[17] M. B. Walker *et al.*, J. Phys. Condens. Matter **6**, 7365 (1994).
[18] K. A. McEwen *et al.*, J. Magn. Magn. Mater. **177–181**, 37 (1998).
[19] N. Lingg *et al.*, Phys. Rev. B **60**, R8430 (1999).
[20] S. W. Zochowski *et al.*, Physica (Amsterdam) **206–207B**, 489 (1995).
[21] Y. Tokiwa *et al.*, J. Phys. Soc. Jpn. **70**, 1731 (2001).
[22] K. A. McEwen *et al.*, J. Magn. Magn. Mater. **140–144**, 1411 (1995).
[23] S. W. Zochowski and K. A. McEwen, Physica (Amsterdam) **199–200B**, 416 (1994).
[24] H. C. Walker *et al.*, Physica (Amsterdam) **378–380B**, 981 (2006).
[25] K. A. McEwen *et al.*, J. Phys. Condens. Matter **15**, S1923 (2003).
[26] M. Blume and D. Gibbs, Phys. Rev. B **37**, 1779 (1988).