# FAST TRACK COMMUNICATION

# Antiferro-quadrupolar structures in UPd₃ inferred from x-ray resonant Bragg diffraction

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**Abstract**
A systematic analysis of resonant x-ray Bragg diffraction data for UPd₃, with signal enhancement at the U $M_{IV}$ edge, including possible structural phase transitions leads to a new determination of the space groups of the material in the phases between $T_0 = 7.8$ K and $T_{+1} = 6.9$ K, as $P222_1$, and between $T_{-1} = 6.7$ K and $T_2 = 4.4$ K, as $P2_1$. In addition, the quadrupolar order parameters, $\langle Q_{ab} \rangle$, inferred from diffraction data for the phase between $T_{-1}$ and $T_2$, are $\langle Q_{xz} \rangle$ and $\langle Q_{yz} \rangle$ at the (103) Bragg reflection and $\langle Q_{xy} \rangle$ at the (104) reflection.

## 1. Introduction

Phase transitions in materials are often driven by a cooperative action among degrees of freedom of the electrons. The paramagnetic–magnetic transition, for example, may arise from interactions between magnetic dipole moments. The potential importance of multipolar, e.g., quadrupolar, interactions in f-electron systems has long been recognized [1–3]. Experimental techniques utilizing resonant x-ray Bragg diffraction (RXS), which have evolved in the past decade, are now the preferred techniques for exposing the interplay of charge, spin and orbital electron degrees of freedom in complex materials. In short, RXS reveals multipoles with a directness of purpose not available with any other technique in the science of materials. By measuring intensities of weak, space group forbidden reflections, families of multipoles can be detected, including, magnetic charge (or magnetic monopole) [4], dipole [5], anapole [6, 7], quadrupole [8], octupole [9, 10] and hexadecapole [11, 12]. Use of resonant x-ray Bragg diffraction to detect some of these strange multipoles hosted by complex materials is quite analogous to atomic parity violation experiments to measure the nuclear anapole [13] and it is the method by which to verify strange multipoles predicted in simulations [14].

A great deal of attention has focused on transition-metal materials especially manganites, in which it has been shown that orbital order is the key to understanding a raft of relevant physical properties [15, 16]. The situation of rare-earth (4f) or actinide (5f) ions is different because the coupling between the spin and orbital angular momentum is relatively strong. High-order multipolar interactions may eventually manifest themselves in other subtle effects, such as lifting the degeneracy between single or multi-k structures, or independently of any magnetic order, the interactions between the 4f shells drive orderings in which their electronic density no longer respects the initial symmetries. In the latter cases, the primary order parameter is not of magnetic nature, but of orbital one. As the additional 4f asphericity is usually well described by the emergence of a quadrupolar arrangement, this modification of the system is called quadrupolar order. The case of multipolar ordering, although its possibility has long been recognized and theoretically investigated, remains a rather esoteric issue mainly because of the limited number of systems that unambiguously display the behaviour [1]. The situation has improved recently because novel experimental findings have been reported for several more rare-earth and actinide compounds [17, 18, 3].

The purpose of this article is to interpret resonant x-ray Bragg diffraction by UPd₃ [19, 20], in particular

the dependence of the intensities of the different super-lattice peaks on sample temperature and sample orientation (azimuthal angle) in terms of the possible lowerings of space group symmetry and their associated quadrupolar structures. The Russell–Saunders coupling scheme yields $S = 1$, $L = 5$, $J = L - S = 4$. The large orbital moment gives rise to a strong coupling to the lattice and hence it is not surprising that this is a system in which quadrupolar effects are dominant. Because the U–U distance, which is around 4.11 Å, is larger than that of the Hill limit (3.6 Å), the system (UPd$_3$) behaves like a localized 4f-system. The low temperature specific heat of UPd$_3$ reveals a contribution from low-lying crystal-field (CF) levels, which gives rise to sharp phase transitions. The order would then result from a delicate balance between rather strong magnetic interactions and CF interactions. The possibility that quadrupolar order occurs in UPd$_3$ was first raised in [21] and reiterated since then.

McEwen and co-workers [22] re-analysed available experimental data for UPd$_3$, and produced both a new energy level scheme, with wavefunctions, for the high temperature phase, and a model for the progression of the phase transitions.

## 2. Calculation of the RXS structure factor

Resonant x-ray Bragg diffraction experiments [19, 20] that we discuss were carried out with the x-ray energy tuned to the M$_{IV}$ edge of U at 3.728 keV. At this edge, the resonant scattering cross-section is dominated by electric dipole (virtual) transitions connecting 3d$_{3/2}$ and 5f$_{5/2}$ electron states. The observation of satellite peaks at the M$_{IV}$ edge of U establishes both that long-range order of the 5f electrons occurs in UPd$_3$ and that these experiments probe ordering of the quadrupolar moments in the 5f shell.

For Bragg diffraction enhanced by an electric dipole event (E1) the unit-cell structure factor, $F$, can be written as a product of a quantity **X**, which describes the condition of the x-rays, and a quantity $\Psi$ that is related to the valence electrons [23]

$$F = \sum_K \mathbf{X}^K \cdot \Psi^K = \sum_{K,Q} (-1)^Q X_{-Q}^K \Psi_Q^K. \quad (1)$$

Here, $K = 0, 1, 2, \ldots$, is the rank of a spherical component and the projection $Q$ takes values within the range $-K < Q < K$. $X_Q^K$ is described in terms of coordinates fixed by the chosen geometry of the experiment, while $\Psi_Q^K$ is written with respect to axes in the crystal. $\Psi_Q^K$, a structure factor of electrons in a unit cell, is a sum of multipoles $\langle T_Q^K \rangle_{\mathbf{d}}$, at sites $\mathbf{d}$ in the unit cell multiplied by the usual spatial phase factors,

$$\Psi_Q^K = \sum_{\mathbf{d}} \exp(i\mathbf{k} \cdot \mathbf{d}) \langle T_Q^K \rangle_{\mathbf{d}}. \quad (2)$$

Point-group symmetry places restrictions on the allowed components of $\langle T_Q^K \rangle$. Measured intensities reveal information on anisotropy in time-even, charge-like ($K$ = even integer) and time-odd, magnetic ($K$ = odd integer) distributions. For scattering enhanced by an E1 event one can observe multipoles with rank $K = 0$ (monopole or charge), $K = 1$ (dipole) and $K = 2$ (quadrupoles).

## 3. Properties of UPd$_3$

At room temperature, the material crystallizes in the double hexagonal close-packed structure (dhcp) $P6_3/mmc$ with U ions at sites with locally quasi-cubic (2a Wyckoff positions) and hexagonal (2d Wyckoff positions) symmetry. The palladium ions are at 6g and 6h positions. Benefiting from the selective character of RXS, Pd ions play no part and the observed RXS intensity is coming from quasi-cubic uranium ions, given the fact that ordered quadrupole moments are predominantly at the quasi-cubic sites [24, 19]. Resonant x-ray diffraction measurements [19, 20] were done at reflections (103) and (104) in ortho-hexagonal axes with lattice constants $a = \sqrt{3}a_{hex}$, $b = a_{hex}$, and $c = c_{hex}$. In order to align crystal coordinates with the x-ray coordinates defined in [23], it is necessary to perform a rotation of coordinates defined by the Euler angles $(\pi, \beta_{10l}, \pi)$ with $\beta_{103} = 108.0°$ and $\beta_{104} = 103.7°$. Measurements in [19] were only done at a fixed azimuthal angle $\psi = 90°$.

Bulk measurements (heat capacity, electrical resistivity, ultra-sounds measurements, magnetic susceptibility, among others) together with x-ray and neutron scattering experiments [24] have revealed up to four quadrupolar phase transitions: $T_0 = 7.8$ K, $T_{+1} = 6.9$ K, $T_{-1} = 6.7$ K and $T_2 = 4.4$ K, being the transitions at $T_0$ and $T_{+1}$ second order and the transitions at $T_{-1}$ and $T_2$ first order. In the latter phase, the antiferroquadrupolar (AFQ) transition is accompanied by the appearance of a small antiferromagnetic dipolar moment.

## 4. A minimal symmetry model structure factor

We start by deriving the consequences of a minimal symmetry model structure factor similar to the one used in [25] and [26], and investigate the possibility of a 2-fold axis of rotation symmetry about the $b$ crystallographic axis. The general structure factor in atomic axes $(\xi, \eta, \zeta)$ with zeta parallel to the crystal $b$-axis, can be written as

$$\Psi_Q^K(\xi, \eta, \zeta) = B_Q^K + D_Q^K, \quad (3)$$

with $B_{-Q}^K = B_Q^K$ and $D_{-Q}^K = -D_Q^K$. Atomic axes $(\xi, \eta, \zeta)$ are related to crystal axes $(a, b, c)$ by a rotation of $\pi/2$ about the $a$-axis. If we calculate the resonant structure factor for rank 2 tensors (quadrupoles) in reflections of the kind (10l) at azimuthal angle of 90°, we obtain,

$$F_{\sigma'\sigma} = \sqrt{\tfrac{3}{2}} B_0^2$$

$$F_{\pi'\sigma} = \text{Re}\, D_1^2 \cos(\beta + \theta) + \text{Im}\, B_1^2 \sin(\beta + \theta)$$

$$F_{\pi'\pi} = \text{Re}\, B_2^2 (2\cos^2\beta - 1) - \frac{1}{\sqrt{6}} B_0^2 \cos 2\theta \quad (4)$$

$$\qquad + \text{Im}\, D_2^2 \sin 2\beta$$

$$F_{\sigma'\pi} = \text{Re}\, D_1^2 \cos(\beta - \theta) + \text{Im}\, B_1^2 \sin(\beta - \theta).$$

Assuming a point symmetry including a 2-fold axis about the $b$-axis, $|Q|$ is an even integer. Thus $B_1^2$ and $D_1^2$ would be forbidden leading to zero intensity in the rotated channels $\pi'\sigma$ and $\sigma'\pi$ at $\psi = 90°$. This is compatible with the RXS

measurements done at 7.1 K [20, 19]. In the measurements done at $T = 5.2$ K, the appearance of intensity in the rotated channel at the azimuthal angle $\psi = 90°$ implies that the 2-fold axis point symmetry about $b$ is no longer present.

## 5. RXS measurements at $T = 7.1$ K

There is evidence that the material undergoes a structural transition to an orthorhombic space group [27, 28]. Among the orthorhombic subgroups of $P6_3/mmc$ compatible with a 2-fold axis of point symmetry along $b$ for uranium ions occupying quasi-cubic sites, we find that $P222_1$ reproduces the azimuthal measurements published in [20]. In $P222_1$ the $(10l)$ reflections became space group allowed, in agreement with the weak non-resonant intensity in the unrotated channel reported in [19]. The quasi-cubic uranium ions were at positions 2c and 2d of $P222_1$. Uranium ions with $z = 1/4$ and $z = 3/4$ are related by a two-fold axis about $c$. The quadrupolar structure factors for the 2c and 2d sites for the reflection $(10l)$ and arbitrary Miller index $l$ are,

$$\Psi_Q^2(10l)_{(2c)} = \exp(i\pi/2l)(1 + (-1)^{l+Q})\langle T_Q^2\rangle_{(2c)}$$
$$\Psi_Q^2(10l)_{(2d)} = -\exp(i\pi/2l)(1 + (-1)^{l+Q})\langle T_Q^2\rangle_{(2d)}. \tag{5}$$

In these structure factors, we use a different set of axes for the multipoles than those used in the previous section, for the axes of $\langle T_Q^2\rangle$ are now aligned with crystal axes $a, b, c$. At the reflection $(10l)$ what is measured is the difference between the quadrupolar moments in the $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ orthorhombic positions, namely, $\langle T_Q^2\rangle_{(0,0,0)} - \langle T_Q^2\rangle_{(\frac{1}{2},\frac{1}{2},0)}$. As they occupy inequivalent Wyckoff positions (2c and 2d) quadrupoles at positions $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ are not related by the space group. A quadrupolar ordering in which $\langle T_Q^2\rangle_{(0,0,0)} = \langle T_Q^2\rangle_{(\frac{1}{2},\frac{1}{2},0)}$ would not be observed at the $(10l)$ reflection.
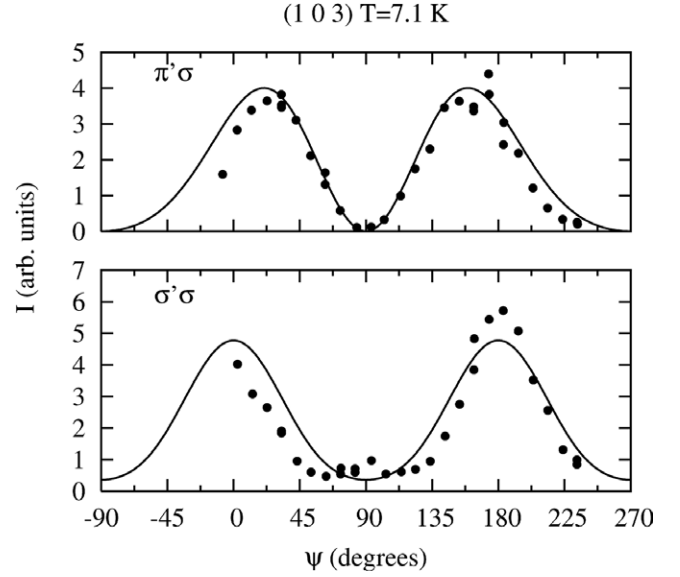
The factor $(1 + (-1)^{l+Q})$ in (5) implies that multipoles $\langle T_Q^2\rangle$ with $|Q| = 1$ are observed in the (103) reflection, while (104) would give access to multipoles with even $|Q|$ ($|Q| = 0, 2$). In addition, point symmetry (with a 2-fold axis about $b$) forces $\langle T_Q^2\rangle$ to be purely real, and this means that in the (103) reflection $\mathrm{Re}\langle T_1^2\rangle \equiv \langle Q_{zx}\rangle$ is observed while at the (104) reflection $\mathrm{Re}\langle T_2^2\rangle \equiv \langle Q_{x^2-y^2}\rangle$ and $\langle T_0^2\rangle \equiv \langle Q_{3z^2-r^2}\rangle$ are observed.

For reflections of the kind $(10l)$ with arbitrary $l$ the total structure factor will be proportional to the difference of multipoles between the two crystal Wyckoff positions, $\langle T_Q^K\rangle_{(2c)} - \langle T_Q^K\rangle_{(2d)}$, i.e., to the difference of the mean values of the multipoles between the sites $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ in orthorhombic coordinates.

The absence of measured resonant intensity at (104) at this temperature [19] implies that $\langle Q_{3z^2-r^2}\rangle$ and $\langle Q_{xz}\rangle$ have no antiferro-ordering. The intensity of (103) reflection is proportional to the difference of $\langle Q_{zx}\rangle$ between the 2c and 2d crystal positions, $\langle Q_{zx}\rangle_{(2c)} - \langle Q_{zx}\rangle_{(2d)}$ and is given by

$$F_{\sigma'\sigma(103)} = -2\langle Q_{zx}\rangle \sin\beta_0 \cos\alpha_0 \tag{6}$$
$$F_{\pi'\sigma(103)} = -\langle Q_{zx}\rangle[\sin(\alpha_0 + \gamma_0 - \theta)(1 + \cos\beta_0)$$
$$\times (2\cos\beta_0 - 1) + \sin(\alpha_0 - \gamma_0 + \theta)(1 - \cos\beta_0)$$
$$\times (2\cos\beta_0 + 1)]. \tag{7}$$



**Figure 1.** Azimuthal variation of the intensity in the (103) reflection measured at $T = 7.1$ K. Experimental points are taken from [20]. The continuous line shows the fit of the data to equations (6) and (7).

The angles $\alpha_0$, $\beta_0$, $\gamma_0$ result from the composition the azimuthal rotation and the rotation that aligns the Bragg wavevector with the x-ray coordinates, and are given by

$$\alpha_0 = \mathrm{arccot}(-\cot\psi \sin\beta)$$
$$\beta_0 = \arccos(\cos\psi \cos\beta) \tag{8}$$
$$\gamma_0 = \mathrm{arccot}(-\cot\beta \sin\psi),$$

with the angle $\beta$ for the (103) and (104) reflections being $\beta_{103} = 108.0°$ and $\beta_{104} = 103.7°$.

The azimuthal dependence of the (103) reflection together with experimental data [20] is depicted in figure 1. We have allowed contribution from a non-resonant (Thomson) term in the $\sigma'\sigma$ channel. The quadrupolar structure depicted in figure 4 of [20] corresponds to the antiferro-quadrupolar ordering of $\langle Q_{xz}\rangle$ observed, i.e. $\langle Q_{xz}\rangle_{(2c)} = -\langle Q_{xz}\rangle_{(2d)}$. A possible contribution of $\langle Q_{x^2-y^2}\rangle$ that would modify the azimuthal dependence of the (103) reflection was proposed in [29]. However, in space group $P222_1$ contribution of $\langle Q_{x^2-y^2}\rangle$ to the (103) reflection is not allowed, as it would have in-phase stacking along the $c$-axis, i.e. when making the translation $(0, 0, \frac{1}{2})$ along z, the value of $\langle Q_{x^2-y^2}\rangle$ would be the same (this is different to the structure depicted in [19] which has antiphase stacking of $\langle Q_{x^2-y^2}\rangle$ along the $c$-axis). Still, in the structure of space group $P222_1$ there would be the possibility of ordering $\langle Q_{x^2-y^2}\rangle$ with $\langle Q_{x^2-y^2}\rangle_{(000)} = \langle Q_{x^2-y^2}\rangle_{(\frac{1}{2},\frac{1}{2},0)}$, which would not be observable in $(10l)$ reflections.

## 6. RXS measurements at $T = 5.2$ K

To accommodate the observed change to the shape of the (103) azimuthal curve, and the appearance of intensity in $\pi'\sigma$ at 90° in the azimuthal curves of both (103) and (104) reflections (see figures 2 and 3), it is necessary to reduce the symmetry
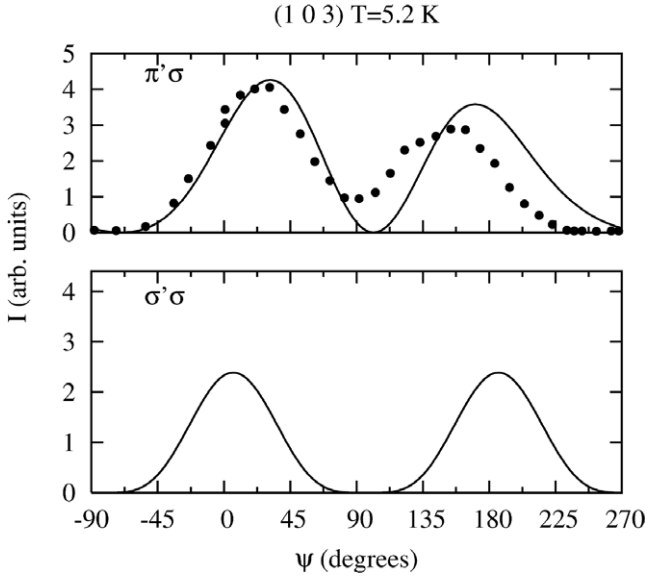
**Figure 2.** Azimuthal variation of the intensity in the (103) reflection measured at $T$ = 5.2 K. Experimental points are taken from [20]. Continuous lines show the fit of the data to equations (9) and (10).

experienced by the quasi-cubic uranium ions (two-fold axis about $b$). Possible subgroups of $P222_1$ that do not break the translational symmetry are $P2_1$, P2 and P1. The possibility of a lowering of symmetry to a monoclinic space group has already been suggested in [28]. The minimum reduction of symmetry to justify these changes would be to consider the monoclinic space group $P2_1$. In this space group, ions at different positions in $z$ within the unit cell continue to be related by a two-fold axis about $c$. The quasi-cubic uranium ions in this group would occupy two different sets of 2a Wyckoff positions. The algebraic form of unit-cell structure factors is unchanged, but now there is no point symmetry and $\langle T_Q^K \rangle$ is no longer purely real. In consequence, there are additional contributions containing $\langle Q_{yz} \rangle$ at (103) and $\langle Q_{xy} \rangle$ at (104). The azimuthal

dependence of the (103) reflection is then:

$$F_{\sigma'\sigma(103)} = -2\sin\beta_0(\langle Q_{zx}\rangle\cos\alpha_0 + \langle Q_{yz}\rangle\sin\alpha_0) \quad (9)$$

$$\begin{aligned}F_{\pi'\sigma(103)} = -\langle Q_{zx}\rangle[&\sin(\alpha_0+\gamma_0-\theta)(1+\cos\beta_0)\\ &\times(2\cos\beta_0-1)+\sin(\alpha_0-\gamma_0+\theta)(1-\cos\beta_0)\\ &\times(2\cos\beta_0+1)]+\langle Q_{yz}\rangle[\cos(\alpha_0+\gamma_0-\theta)(1+\cos\beta_0)\\ &\times(2\cos\beta_0-1)-\cos(\alpha_0-\gamma_0+\theta)(1-\cos\beta_0)\\ &\times(2\cos\beta_0+1)],\end{aligned} \quad (10)$$
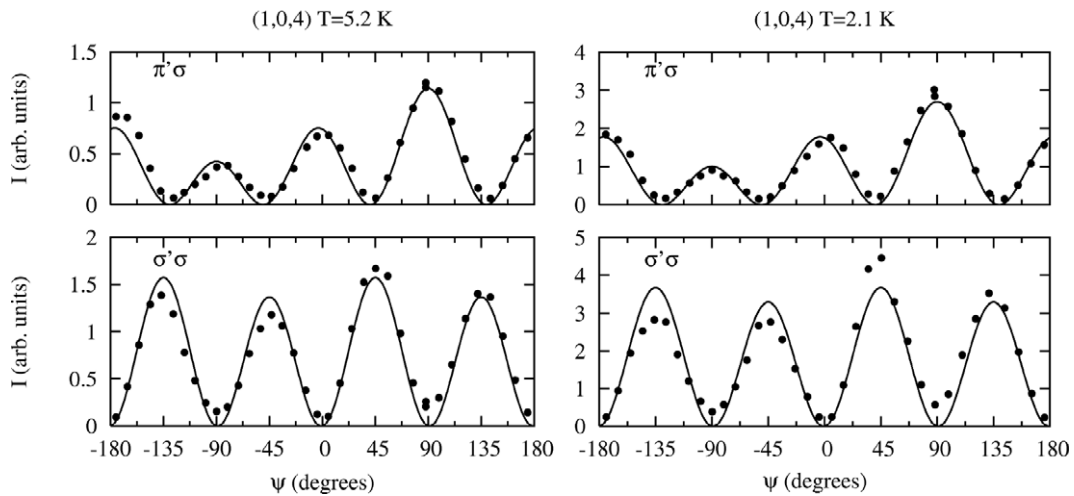
and for the (104) reflection,

$$\begin{aligned}F_{\sigma'\sigma(104)} = &\langle Q_{zz}\rangle(3\cos^2\beta_0-1)\\ &+2\sin^2\beta_0(\tfrac{1}{2}(\langle Q_{xx}-Q_{yy}\rangle)\cos2\alpha_0\\ &+\langle Q_{xy}\rangle\sin2\alpha_0)\end{aligned} \quad (11)$$

$$\begin{aligned}F_{\pi'\sigma(104)} = &-\tfrac{3}{2}\langle Q_{zz}\rangle\sin2\beta_0\sin(\gamma_0-\theta)+\sin\beta_0(1+\cos\beta_0)\\ &\times\{\tfrac{1}{2}(\langle Q_{xx}-Q_{yy}\rangle)\}[(1+\cos\beta_0)\sin(2\alpha_0+\gamma_0-\theta)\\ &+(1-\cos\beta_0)\sin(2\alpha_0-\gamma_0+\theta)]\\ &-\langle Q_{xy}\rangle[(1+\cos\beta_0)\cos(2\alpha_0+\gamma_0-\theta)\\ &+(1-\cos\beta_0)\cos(2\alpha_0-\gamma_0+\theta)]\}.\end{aligned} \quad (12)$$

Figure 2 shows the fitting of the available data for (103) [20] with $\langle Q_{zx}\rangle$ and $\langle Q_{yz}\rangle$ in (9) and (10) allowed to be different from zero, together with the other quadrupoles. The value of $\langle Q_{zx}\rangle/\langle Q_{yz}\rangle$ from the fitting is $\langle Q_{zx}\rangle/\langle Q_{yz}\rangle = -4.72\pm0.12$. Measurements done with $\pi$ incident polarization [19] show that at $T$ = 5.2 K, at $\psi$ = 90°, in (103) $\pi'\pi$ is about one order of magnitude more intense than $\sigma'\pi$ (with our derived parameters we obtain $I_{\pi'\pi}/I_{\sigma'\pi}$ = 19.4 at $\psi$ = 90° and $I_{\pi'\pi}/I_{\sigma'\pi}$ = 8.3 at $\psi$ = −90°). This differs from the fit done in [20], which attributed the variation in the azimuthal dependence in (103) at 5.2 K solely to the contributions of $\langle Q_{xy}\rangle$ and $\langle Q_{x^2-y^2}\rangle$. In our proposed structure these two quadrupoles have in-phase stacking along the $c$-axis and do not contribute to (103) reflection.

Available data [20, 30] for the (104) reflection is shown in figure 3 together with the azimuthal dependence calculated from (11) and (12) with only $\langle Q_{xy}\rangle$ allowed to be different from zero and a non-resonant contribution (Thomson) in $\sigma'\sigma$



**Figure 3.** Azimuthal variation of the intensity in the (104) reflection measured at $T$ = 5.2 and 2.1 K. Experimental points are taken from [30]. Continuous lines show the fit of the data to equations (11) and (12).
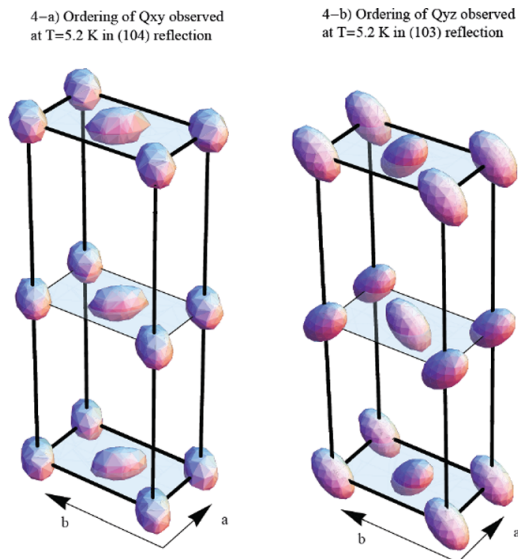
**Figure 4.** Antiferro-quadrupolar orderings of $\langle Q_{xy} \rangle$ and $\langle Q_{yz} \rangle$ observed in the (104) and (103) reflections at $T = 5.2$ K.
(This figure is in colour only in the electronic version)

that is independent of the azimuthal angle. Inclusion of $\langle Q_{x^2-y^2} \rangle$ and $\langle Q_{zz} \rangle$ does not lead to a significant improvement in the fit to (104) data. Moreover, in the case of the (104) reflection measurements done with $\pi$ incident polarization at $T = 5.2$ K [19] show a very weak intensity in the $\pi'\pi$ channel and both $\langle Q_{x^2-y^2} \rangle$ and $\langle Q_{zz} \rangle$ give a non-zero intensity at $\psi = 90°$ in $\pi'\pi$. However, an accidental cancellation could occur if $\langle Q_{xx} - Q_{yy} \rangle = 3\langle Q_{zz} \rangle$.

Figure 4 shows the antiferro-quadrupolar orderings of $\langle Q_{yz} \rangle$ and $\langle Q_{xy} \rangle$ derived from the proposed space group structure, which are compatible with data collected for the (103) and (104) reflections at $T = 5.2$ K and coexist with the ordering of $\langle Q_{zx} \rangle$ observed at 7.1 K [20]. The stacking along the $c$-axis of the $\langle Q_{yz} \rangle$ component of the quadrupolar moment shown in figure 4(a) changes sign when making a translation of $1/2$ of the z coordinate, which is different to the $\langle Q_{yz} \rangle$ stacking used in [20, 30].

## 7. Conclusions

Resonant x-ray Bragg diffraction data are evidence of an antiferro-quadrupolar ordering in UPd$_3$. Our analysis of available data identifies the space group for the phase between $T_0 = 7.8$ K and $T_{+1} = 6.9$ K as $P222_1$. Additionally, we can infer the quadrupole components $\langle Q_{\alpha\beta} \rangle$ ($\alpha, \beta = x, y, z$) and their stacking pattern contributing to different space group forbidden reflections. Intensity in the (103) reflection is here assigned to the $\langle Q_{zx} \rangle$ quadrupole. For the phase below $T_{-1} = 6.7$ K, measurements are compatible with the space group $P2_1$, which implies loss of the 2-fold axis of rotation symmetry in the point symmetry sites used by the U ions. However, we should be cautious with this assignment of space group, given that the phase transition at $T_{-1}$ is first order and in that case the low temperature space group is not necessarily a subgroup of $P222_1$. The intensity at the (103) reflection would come

mainly from $\langle Q_{zx} \rangle$ together with a small $\langle Q_{yz} \rangle$ contribution. Intensity at (104) is attributed to $\langle Q_{xy} \rangle$ with a possible small contributions from $\langle Q_{x^2-y^2} \rangle$ and $\langle Q_{zz} \rangle$. Within the derived structures for both phases of the compound, no additional contributions from other quadrupolar parameters are present in (103) and (104) reflections.

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