Symmetry analysis of quadrupolar and structural ordering in single-q phases of UPd3

W Sikora1, F Białas2, L Pytlik1 and J Malinowski1
1 Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, al. Mickiewicza 30, 30-059 Krakow, Poland
2 Nowy Sacz School of Business - National Louis University, Nowy Sacz, Poland
E-mail: sikora@novell.ftj.agh.edu.pl

Abstract. The paper describes the application of symmetry analysis to construction of possible quadrupolar ordering modes in a crystal with a given space group symmetry. The matrix representing a given tensor property (e.g. quadrupolar moment) is converted to a vector form, for which the standard symmetry analysis algorithms can be applied. The possible ordering modes are obtained as linear combinations of basis vectors of irreducible representations of a given space group, but taking into account the constraints, specific for a given physical quantity (e.g. symmetric matrix form and zero trace for quadrupolar tensors). The results are applied to the single-q phases of UPd3 compound. For completeness the possible structural ordering modes are also calculated, which are consistent with the symmetry of a given quadrupolar ordering.

1. Introduction
In the present paper the ordering of quadrupolar tensor components and possible deformation of the initial potential shape in a quadrupolar phase transition are investigated by the symmetry analysis method [1]. The components of quadrupolar moment tensor (QMT) are calculated from the charge density distribution by the respective textbook formula. The matrix of QMT is always symmetrical and additionally in orthogonal coordinate systems traceless. The QMT matrix can be brought to the principal axes, which may be treated as a local symmetry-adapted coordinate system. Then the matrix of QMT takes the simplest form: only three values on the diagonal can be nonzero and only two of them are independent. For an initial spherical potential shape the QMT form defines the directional deviations from the spherical form, resulting from the presence of nonzero quadrupolar moment.

The quadrupolar ordering concept is intended to characterize, at all atomic positions in the crystal, the spatial shape of the surface associated with the quadrupolar potential (or the surface associated with the deformed total potential) and the orientation of QMT’s principal axes in relation to the crystallographic system. The signs of QMT coefficients characterize the type of deformation and their values characterize the magnitude of the potential surface deformation. By the symmetry analysis method all types of quadrupolar ordering, allowed for a given parent structure, are calculated, together with their resulting final symmetry groups. An additional analysis can be also carried out to determine the possible patterns of atomic displacements of the neighboring atoms, which are consistent with the symmetry imposed by the quadrupolar ordering.
In the present work the method is applied to quadrupolar moment ordering of U atoms and possible patterns of atomic displacements of the neighboring Pd atoms in the hexagonal UPd₃ compound. The high-temperature structure of UPd₃ - the parent structure - is described by the hexagonal space group \(P6_3/mmc\) (\(D_{6h}^4\)) and it is isostructural to Ni₃Ti structure [11]. The atomic positions found from the diffraction experiments are as follows: four uranium atoms are located in quasi-cubic 2(a) sites: U1(0,0,0), U2(0,0,1/2) and hexagonal 2(c) sites: U3(1/3,2/3,1/4), U4(2/3,1/3,3/4) while the twelve palladium atoms are located in 6(h) and 6(g) sites [5,12]. The experimental data from neutron and X-ray diffraction, [2,3] as well as measurements of heat capacity, thermal expansion, ultrasound attenuation [4], \(\mu\)SR [5], magnetic susceptibility [6] indicate that a sequence of phase transitions is encountered at temperatures \(T_0=7.6\,\text{K}, T_+1=6.9\,\text{K}, T_-1=6.7\,\text{K}\) and \(T_2=4.4\,\text{K}\). The analysis of diffraction data (neutrons, X-rays) indicates that below \(T_0\) various forms of antiferroquadrupolar ordering are present, together with the accompanying structural changes, and that some form of antiferroquadrupolar ordering coexists with antiferromagnetic ordering below \(T_2\) [2,6]. The non-zero quadrupolar moments are found mainly for the U atoms located in the quasi-cubic 2(a) sites. In the quadrupolar phase the ordering vector is found to be \(k=(1/2,0,0)\) and principal axes of the quadrupolar moments coincide with orthorhombic coordinate system axes. Below \(T_-1\) a deflection of the quadrupolar moments from the coordinate system axes is observed [5]. Additionally there is a suggestion [4,7] that both phases below \(T_-1\) exhibit the so called triple-q structure in order to avoid anti-phase domain walls and that the associated phase transitions at \(T_-1\) and \(T_2\) are of the first order, what possibly breaks the group-subgroup relation with the parent hexagonal phase.

The present paper deals with the possible types of quadrupolar ordering modes in the two single-q phases (\(T_-1<T<T_0\)), the resulting final symmetry groups, and the possible patterns of atomic displacements of the neighboring Pd atoms, which are consistent with the symmetry imposed by the quadrupolar ordering. The models of ordered structure and discussion of corresponding sets of free parameters calculated from symmetry considerations are compared with the results of experimental investigations.

2. Elements of the symmetry analysis

2.1. Description of the ordering pattern. The symmetry analysis method, used for construction of the ordering pattern, is known for a long time and it works properly if some conditions are fulfilled [1]. The symmetry change should preserve the group – subgroup relation between the initial and the final phase and the described property should be localized on some set of equivalent positions in the unit cell of the initial phase. The property can be represented by a scalar, vector (polar or axial) or tensor quantity.

The method itself has been derived from the theory of group and representations and is based on the decomposition of full (permutational, , mechanical, magnetic, or quadrupolar) representation of the crystal space group, calculated for a given wave vector \(k\) and a given orbit of positions, into its irreducible representations (IR-s). Such a decomposition allows calculation of the so called basis vectors (BV-s) attributed to each IR, i.e. vectors which under the action of symmetry operations transform according to the respective IR. The final ordering pattern of the investigated property is built up as a linear combination of basis vectors attributed to one or more irreducible representations. Thus the global vector \(\vec{S}\), describing the considered local property \(\hat{a}\) in the whole crystal can be written as:
\[ S^{(k_L)} = \begin{bmatrix}
\hat{a}(r_1) \\
\vdots \\
\hat{a}(r_n)
\end{bmatrix} = \sum_{k_L} \sum_{v, \lambda} C_{v, \lambda}^{(k_L)} \begin{bmatrix}
\Psi_{v, \lambda}^{(k_L)}(r_1) \\
\vdots \\
\Psi_{v, \lambda}^{(k_L)}(r_n)
\end{bmatrix} e^{i\mathbf{k}_L \cdot \mathbf{r}_{p,q,s}} \]

where the sum on the right-hand side runs over \{k_L\}, denoting one or more wave vectors describing the ordering. The other summation indices \(v, \lambda\), denote respectively the IR label and an additional index, numbering the basis vectors belonging to the given \(v\)-th IR. The symbols \(\Psi_{v, \lambda}^{(k_L)}\) denote the parts of the respective basis vectors, calculated for atom \(i\), for a given wave vector \(k_L\). The translation vector \(\mathbf{r}_{p,q,s} = p\mathbf{a}_1 + q\mathbf{a}_2 + s\mathbf{a}_3\) runs over all unit cells of the crystal, when the indices \(p, q, s\) scan the set of integer numbers. As can be noticed the translation of the individual site \(r_n\) by the lattice vector \(\mathbf{r}_{p,q,s}\) is equivalent to multiplication of the local part of the respective basis vector by a factor \(\exp(i\mathbf{k}_L \cdot \mathbf{r}_{p,q,s})\). Taking this into account one can focus attention on the single-site description of the property \(\hat{a}\) :

\[ a_\alpha^{(k_L)}(r_n) = a^{(k_L)}_{\alpha} = \sum_{k_L} \sum_{m} C_{m}^{(k_L)} \Psi^{(k_L)}_{m, \alpha}(r_n) \]

where \(\alpha\) labels the components of \(\hat{a}\) at the local site and the new sum index \(m \equiv v, \lambda\) numbers the consecutive basis vectors used in the linear combination.

As shown above construction of ordering mode requires the exact knowledge of basis vectors attributed to individual irreducible representations of a given space group for all the wave vectors contributing to the ordering pattern. There are several software packages that can be used for such calculations. The basic application written and used by the authors of the present paper is the MODY program [8].

The local description of a given property, denoted here as \(\hat{u}\), can be a vector (displacement, magnetic moment) or a scalar (electron density, probability), which is in fact a reduced, one element vector. Therefore the regular, well-known symmetry analysis has been elaborated for vector quantities. In order to apply the whole algorithm to tensor quantities (e.g. electric or magnetic quadrupolar moment) a special procedure has to be applied, transforming both the matrix representing the local tensor quantity \(\hat{u}(r_n)\) and the transformation matrices. The tensor 3x3 matrix is transformed into a nine element vector with the new vector element index \(r\) calculated as: \(r = 3(i-1)+j\). If the same index recalculation procedure is applied to the transformation matrices the well-known vector algorithm can be applied directly [9].

2.2. The constraints imposed on the solution. The coefficients of the linear combination \(C^{(k_L)}\) are the objects, which in fact specify the exact form of the global ordering pattern. In principle they should be arbitrary, as they explore the freedom left after imposing the symmetry requirements. However there are additional conditions that have to be fulfilled, if the solution for \(S^{(k_L)}\) is to represent a given physical quantity. For most vector quantities (displacement, magnetic moment) the basic requirement is that all the components of \(\hat{u}\) should be real, even if the basis vector used for construction of the solution are complex. The respective equation takes the form:

\[ S^{(k_L)} = \begin{bmatrix}
\hat{a}(r_1) \\
\vdots \\
\hat{a}(r_n)
\end{bmatrix} = \sum_{k_L} \sum_{v, \lambda} C_{v, \lambda}^{(k_L)} \begin{bmatrix}
\Psi_{v, \lambda}^{(k_L)}(r_1) \\
\vdots \\
\Psi_{v, \lambda}^{(k_L)}(r_n)
\end{bmatrix} e^{i\mathbf{k}_L \cdot \mathbf{r}_{p,q,s}} \]
\[ \text{Im}(\hat{u}_{i,\alpha}^{(k)}) = 0 \quad \forall i, \alpha \]  

For tensor quantities the detailed constraints depend on the exact nature of the physical quantity. For moment of inertia tensor the only requirement would be the symmetric form of the matrix, for electric quadrupolar moment tensor an additional condition is the zero trace of the matrix. The respective equations look as follows:

\[ u^{(k_1)}_{i,12} = u^{(k_2)}_{i,21} \quad u^{(k_1)}_{i,13} = u^{(k_2)}_{i,31} \quad u^{(k_1)}_{i,23} = u^{(k_2)}_{i,32} \quad u^{(k_1)}_{i,11} + u^{(k_2)}_{i,22} + u^{(k_2)}_{i,33} = 0 \quad \forall i \]  

The above requirements generate a set of equation for the unknown \( C^{(k)}_{m} \) coefficients, and after solving this equation set the final solution can be written. It usually happens that even after imposing the constraints there are still some free parameters left, like the amplitude or phase of the ordering mode, the number of which depends on the irreducible representations used for construction of the solution.

3. Quadrupolar ordering concept

3.1. Quadrupolar potential contribution and its visualisation. The quadrupolar ordering concept is intended to characterise the electric potential and electron density distribution at individual atomic positions in the crystal. In particular it is intended to describe:

- orientation of principal axes of quadrupolar moment tensor (QMT) in relation to the crystallographic system axes
- the spatial shape of quadrupolar potential, related to the values of QMT components

The expansion of electric potential from any local atomic charge distribution may be written as:

\[ \Phi(r) = \Phi_m(r) + \Phi_d(r) + \Phi_q(r) + \ldots \]  

where the \( m,d \) and \( q \) indices denote the monopolar, dipolar and quadrupolar contributions to the total potential. The shape of the potential and charge distribution around the local crystal site and depends on the relative contributions from the individual terms of the expansion. It is often assumed that for zero external field conditions the dipolar contribution is negligible and the shape of local charge and potential distributions is controlled by the quadrupolar contribution, as the monopolar contribution is fully symmetric. The quadrupolar contribution can be characterized by its expansion into spherical functions [10]. Such expansion has been used for visualization of the angular dependence of both the quadrupolar potential contribution and the total potential. The analyzed potential values are calculated for a fixed distance from the local center \( (r_0 = \text{const}) \). In the program Tensor_Vis by J. Malinowski [9] the potential value for a given set of spherical angles \( (\theta, \phi) \) is translated into the radial distance from the center, thus graphically reflecting the spatial shape of the potential distribution. All the potential shape pictures found below have been produced using that program.

3.2. Properties of quadrupolar moment tensor matrix The components of quadrupolar moment tensor (QMT) in orthogonal coordinate systems are usually defined as [10]:

\[ Q_{ij} = \int (3x_j x_i - \rho^2 \delta_{ij}) q(\rho) d^3x \]  

The definition implies two properties for QMT matrix: it is always symmetric i.e. \( Q_{ij} = Q_{ji} \) and its the trace is always zero i.e. \( Q_{33} = -Q_{11} - Q_{22} \). The general form of the QMT matrix can always be transformed to the diagonal form by transformation to the local coordinate system oriented along the so called principal axes of QMT tensor. The general and diagonal forms of QMT look respectively as below:
The general form of QMT suggests that there should be five arbitrary parameters, but the transformation to diagonal form shows that there are only two parameters characterizing the shape of the potential itself: $Q_a$ and $Q_b$. The other three parameters characterize the spatial orientation of the potential (electron density) shape. It should be stressed that the presence of two free parameters is a direct proof that not all shapes of the electron density cloud (potential) can be described by a prolate or oblate spheroid.

$$Q_{gen} = \begin{pmatrix} Q_{11} & Q_{12} & Q_{13} \\ Q_{12} & Q_{22} & Q_{23} \\ Q_{13} & Q_{23} & -Q_{11} - Q_{22} \end{pmatrix} \quad Q_{diag} = \begin{pmatrix} Q_a & 0 & 0 \\ 0 & Q_b & 0 \\ 0 & 0 & -Q_a - Q_b \end{pmatrix}$$ (7)

The QMT matrix components can be used for calculation of the expansion coefficients in the potential expansion into spherical functions. The necessary relations can be found in [10] and they have been used to produce the values of quadrupolar contribution to the potential, later used for its visualization. A direct illustration of such visualization can be found in Figure 1. The diagonal forms of QMT can be classified with respect to the signs and relative values of the $Q_a$ and $Q_b$ parameters, and the resulting shapes can be attributed to the well-known classification quadrupolar operators $Q_{\alpha,\beta}$. For example the QMT matrix in Figure 1 and the corresponding shapes of the quadrupolar and total potential surfaces can be attributed to the operator combination labeled as $(Q_{x^2-y^2} + Q_{yz})$.

4. Results of the symmetry analysis of quadrupolar ordering

Symmetry analysis of the quadrupolar ordering applied to the parent structure with the $P 6_3/mmc$ symmetry group and U quadrupolar moments localized on 2(a) positions indicates, that these positions belong to one orbit of the wave vector group G(k) for the ordering vector $k=(1/2,0,0)$. All irreducible representations for that $k$ vector are real and one-dimensional. IR-s that are potentially active in the quadrupolar phase transition are contained in the full representation decomposition for U(2a) positions: $\tau_1$ and $\tau_3$ - five times each, $\tau_4$ and $\tau_7$ – four times each. It means, that we have five different basis vectors, which transform according to the $\tau_1$ representation, and which may be used in the linear combination, to produce a quadrupolar structure solution leading to high final orthorhombic $P mma$ symmetry, corresponding to this representation. The similar situation occurs for $\tau_3$, leading to quadrupolar structure with the $P nmn$ symmetry group, which differs from the $\tau_1$ structure by the sign of the QMT at the U2 site. For IR $\tau_3$ we have four different basis vectors, which may be used in the linear combination, leading to the structure with $P nma$ symmetry group. The same situation occurs for $\tau_4$, leading to a structure for which the QMT signs at U(2) sites are opposite to the respective signs in $\tau_3$ structure, and which exhibits the $P bcn$ symmetry group.
The full representation decomposition for U(2c) positions contains: IR-s \( \tau_1 \) and \( \tau_8 \) - three times each, and IR-s \( \tau_2, \tau_3, \tau_4, \tau_5, \tau_6 \) and \( \tau_7 \) - two times each. The representations in QMT ordering at U(2c), which are possibly present also for QMT ordering at U(2a) are: \( \tau_1, \tau_3, \tau_5 \) and \( \tau_7 \).

The BV functions calculated by the MODY program for \( P_{6/mmc} \) group are given in the non-orthogonal, hexagonal setting. Therefore the linear combinations of basis vectors are also calculated in the hexagonal system. For discussion of the minimal number of relevant free parameters in the final solution, i.e. after applying the conditions imposed on the coefficients of the linear combination and for drawing the shape of potential it is convenient to transform these functions to the orthogonal system. Therefore for the discussion of solutions the orthorhombic system is naturally chosen, in the setting related to the orthorhombic cell of the structure after phase transition.

For U(2a) IR-s \( \tau_1 \) and \( \tau_5 \) the five unknown coefficients \( C_m \) (\( m=1,5 \)) of the linear combination in the hexagonal system are treated as free parameters \((A,B,C,D,E)\). The conditions imposed on the solution require that the parameters have to be related by the following equations: \( A-B/2+E=0 \) and \( C=D \). As can be seen from these equations two groups of parameters may be regarded independently: \((A,B,0,0,E)\) and \((0,0,C,D,0)\). The same types of QMT structures, which correspond to these two groups of parameters, are found for QMT solutions at U(2c) sites, but in the (2c) case the respective parameter sets are attributed to different IR-s.

Table 1a. The characteristic types of U(2a) QMT solutions for IR \( \tau_1 \) and parameter set \((A,B,0,0,E)\), (valid also for U(2c) solutions for IR \( \tau_8 \) and parameter set \((A',B',E')\) )

| Coefficients of linear combinations | QMT matrix in hexagonal setting \( Q(1)=Q(2) \) | QMT matrix in orthogonal setting \( Q(1)=Q(2) \) | Angular distribution of \( \Phi_q \) | Directions of principal axes |
|-------------------------------------|-----------------------------------------------|-----------------------------------------------|------------------------------------------|-------------------------------|
| \( A=-2Q \)                        | \( \begin{pmatrix} -2Q & -Q & 0 \\ -Q & 0.25Q & 0 \end{pmatrix} \) | \( \begin{pmatrix} 0.75Q & 0 \\ 0 & 0 \end{pmatrix} \) | Fig.2a                                  | \( [2 \ 1 \ 0]_{\text{h}} \) |
| \( B=-2.5Q \)                      |                                                                 |                                                                 | \( [0 \ 1 \ 0]_{\text{h}} \) | \( [0 \ 0 \ 1]_{\text{h}} \) |
| \( E=0.75Q \)                      | \( \begin{pmatrix} 0 & 0.25Q & 0 \end{pmatrix} \) |                                                                 |                                                                 |                               |
| \( A=Q \)                          | \( \begin{pmatrix} Q & 0.5Q & 0 \end{pmatrix} \) | \( \begin{pmatrix} 0.75Q & 0 \\ 0 & 0 \end{pmatrix} \) | Fig.2b                                   | \( [2 \ 1 \ 0]_{\text{h}} \) |
| \( B=2Q \)                         | \( \begin{pmatrix} 0.5Q & -0.5Q & 0 \end{pmatrix} \) |                                                                 | \( [0 \ 1 \ 0]_{\text{h}} \) | \( [0 \ 0 \ 1]_{\text{h}} \) |
| \( E=0 \)                          | \( \begin{pmatrix} 0 & 0 & 0 \end{pmatrix} \) |                                                                 |                                                                 |                               |

The characteristic types of quadrupolar structures for these types of parameter sets are given in the Table 1a and Table 1b correspondingly. The axis shown in boldface in the last column denotes that QMT principal axis, which is also the full rotation symmetry axis of the deformed potential, or the direction where deformation of spherical potential is zero. The amplitude parameter \( Q \) changes only the amplitude of deformation, without changing the type of potential shape or directions of QMT principal axes. As shown in Table 1a, essentially different choices of \( A,B,E \) parameters, which all fulfill the equation (4) condition, lead to quadrupolar orderings with QMT principal axes directed along the other two axes of orthogonal system. The respective solutions at U(2a) for \( \tau_5 \) are different by the QMT sign at the U2 site. The same types of solutions are obtained for U(2c) sites, but the one which corresponds to IR \( \tau_5 \) and \( (A,B,0,0,E) \) at U(2a) is attributed to \( \tau_1 \) and \( (A',B',E') \) at U(2c), while the one corresponding to \( \tau_5 \) and \( (0,0,C,D,0) \) at U(2a) is attributed to \( \tau_4 \) and \( (C',D') \) at U(2c).
Table 1b. The characteristic types of U(2a) QMT solutions for IR $\tau_1$ and parameter set $(0,0,C,D,0)$ (valid also for U(2c) solutions for IR $\tau_5$ and parameter set $(C',D')$)

| Atom   | QMT matrix in hexagonal setting $Q(1)= -Q(2)$ | QMT matrix in orthogonal setting $Q(1)= -Q(2)$ | Angular distribution of $\Phi_q$ | Directions of principal axes |
|--------|---------------------------------------------|---------------------------------------------|-------------------------------------|-------------------------------|
| U1 $(0,0,0)$, $C=D=Q$ | $\begin{bmatrix} 0 & 0 & Q \\ 0 & 0 & 0.5Q \\ Q & 0.5Q & 0 \end{bmatrix}$ | $\begin{bmatrix} 0 & 0 & \sqrt{3}Q/2 \\ 0 & 0 & 0 \\ \sqrt{3}Q/2 & 0 & 0 \end{bmatrix}$ | Fig.2c | $[0 \ 1 \ 0]_h \ [0 \ 1 \ 0]_o$ |

Figure 2. The angular distributions of $\Phi_q$ and $\Phi$ for IR $\tau_1$ and the following parameter sets: a) $(-2Q,-2.5Q,0.75Q)$; b) $(Q,2Q,0,0,0)$; c) $(0,0,Q,0,0,0)$.

For U(2a) QMT solutions for IR $\tau_3$ and $\tau_7$ the sets of four parameters ($A',B',C' D'$) in the hexagonal system, which fulfill the Eq.(4) conditions, have to obey the following equations: $A'=C'$ and $B'=D'$. Now it can be seen that the following parameter sets may be considered independently: $(A',0,A',0)$ and $(0,B',0,B')$. Also in this case the types of U(2a) QMT structures, which correspond to these two groups of parameters, are similar to QMT solutions at U(2c) sites, but again in (2c) both cases are attributed to different IR-s.

The characteristic types of QMT structures for these parameter sets and for their combination $(A',B',A',B')$ are given in the table 2. The respective solutions for IR $\tau_7$ are different only by the QMT sign at the U2 site. The same type of solutions are obtained for U(2c) sites, but the one corresponding to IR $\tau_7$ and $(A',0,A',0)$ at U(2a) sites is attributed to IR $\tau_3$ and $(A',A')$ at U(2c), and the solution type which belongs to $\tau_7$ and $(0,B',0,B')$ at U(2a) sites is attributed to $\tau_2$ and $(B',B')$ at U(2c) sites.
Table 2. The characteristic types of U(2a) QMT solutions for IR \(\tau_3\), and parameter set \((A,B,A,B)\) (valid also for U(2c) QMT solutions for IR-s \(\tau_6\) and \(\tau_7\)) and independent parameter sets \((A,0,A,0)\) and \((0,B,0,B)\)

| Coefficients of linear combinations | QMT matrix in hexagonal setting | QMT matrix in orthogonal setting | Angular distribution of \(\Phi_q\) | Direction of principal axes |
|-------------------------------------|--------------------------------|---------------------------------|-------------------------------|-----------------------------|
| \(p=(A;B;A;B)\) \(\text{U(2a)}: \tau_3\) \(\text{U(2c)}: \tau_6+\tau_7\) | \[
\begin{bmatrix}
0 & A & 0 \\
A & A & -B \\
0 & -B & 0
\end{bmatrix}
\] | \[
\begin{bmatrix}
0 & \sqrt{3}A/2 & 0 \\
\sqrt{3}A/2 & 0 & -B \\
0 & -B & 0
\end{bmatrix}
\] | Fig.3a | \([k 0 l]_0\) |
| \(p=(A;0;A;0)\) \(\text{Q(1)}=\text{Q(2)}\) \(\text{U(2a)}: \tau_3\) \(\text{U(2c)}: \tau_6\) | \[
\begin{bmatrix}
0 & A & 0 \\
A & A & 0 \\
0 & 0 & 0
\end{bmatrix}
\] | \[
\begin{bmatrix}
0 & \sqrt{3}A/2 & 0 \\
\sqrt{3}A/2 & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}
\] | Fig.3b | \([0 0 1]_0\), \([1 1 0]_0\) |
| \(p=(0;B;0;B)\) \(\text{Q(1)}=\text{-Q(2)}\) \(\text{U(2a)}: \tau_3\) \(\text{U(2c)}: \tau_7\) | \[
\begin{bmatrix}
0 & 0 & 0 \\
0 & 0 & -B \\
0 & -B & 0
\end{bmatrix}
\] | \[
\begin{bmatrix}
0 & 0 & 0 \\
0 & 0 & -B \\
0 & -B & 0
\end{bmatrix}
\] | Fig.3c | \([1 0 0]_0\), \([0 1 1]_0\), \([0 1 -1]_0\) |

Figure 3. The angular distribution of \(\Phi_q\) and \(\Phi\) for \(\tau_3\) and sets of coefficients: a) \((A,B,A,B)\); b) \((A,0,A,0)\), c) \((0,B,0,B)\)

The symmetry analysis calculations carried out for different arms of the k-vector star \((k_2=(0,1/2,0))\) and \((k_3=(-1/2,1/2,0))\) lead to quadrupolar structures, which are simply different domain orientations of the structures proposed for the \(k_1=(1/2,0,0)\) and described above.
5. Symmetry analysis of the accompanying structural deformations

The structural deformations, accompanying the quadrupolar ordering, should exhibit the same final symmetry, i.e. they should be described by the same active IR-s. The decomposition of reducible mechanical (crystal) representation carried out for U atoms localized at 2(a) positions of \( P \ 63/mmc \) group, with the same \( k \)-vector as for quadrupolar ordering indicates, that the IR-s active in these structural changes are \( \tau_2, \tau_4, \tau_6, \) and \( \tau_8 \). None of them appears as representation possibly active in the quadrupolar ordering. It indicates, that the displacements of U(2a) atoms are not directly associated with quadrupolar phase transition. For U(2c) sites the possible active representations are \( \tau_1, \tau_3, \tau_5 \), but only \( \tau_1 \) and \( \tau_3 \) are shared with the quadrupolar ordering. The respective displacements of U(2c) atoms are shown in Table 4c.

Table 3a. Splitting of 6(h) positions on two orbits in G(k), and corresponding IR-s active in the structural deformations

| Orbit | Atoms position | Active representations |
|-------|----------------|------------------------|
| 1     | Pd1 \((x,2x,0.25)\) | Pd2 \((1-x,1-2x,0.75)\) | \(2\tau_1,2\tau_3,2\tau_4\) |
|       | Pd3 \((1-x,x,0.75)\) | Pd4 \((x,1-x,0.25)\) | \(\tau_5,2\tau_6,\tau_7,2\tau_8\) |
| 2     | Pd5 \((1-2x,1-x,0.25)\) | Pd6 \((2x,x,0.75)\) | \(\tau_1,\tau_3,\tau_4,\tau_5,\tau_6,\tau_8\) |

Table 3b. Splitting of 6(g) positions on two orbits in G(k), and corresponding IR-s active in the structural deformations

| Orbit | Atoms position | Active representations |
|-------|----------------|------------------------|
| 1     | Pd1 \((0.5,0,0)\) | Pd2 \((0.5,0,0.5)\) | \(3\tau_1,3\tau_3\) |
|       | Pd3 \((0.5,0.5,0)\) | Pd4 \((0.5,0.5,0.5)\) | \(3\tau_5,3\tau_7\) |
| 2     | Pd5 \((0,0.5,0)\) | Pd6 \((0,0.5,0.5)\) | \(2\tau_2,2\tau_4,\tau_6,2\tau_8\) |

The atoms of Pd located at 6(h) and 6(g) positions in the parent \( UPd_3 \) structure split into two orbits in the \( G(k_1) \) group. They are given in Table 3a and Table 3b, together with corresponding active IR-s. The active IR-s common for Pd displacements and quadrupolar ordering are \( \tau_1, \tau_3, \tau_5 \) and \( \tau_7 \). Because these representations are real and one dimensional, the BV-s calculated by the MODY program give directly the possible displacements of Pd atoms leading to the structures with the symmetry groups discussed earlier for the quadrupolar ordering. They are listed in the Table 4a and 4b.

Table 4a. Possible displacements of Pd atoms at 6(h) sites for \( k=(1/2,0,0) \) accompanying the quadrupolar ordering

| IR | Version | Orbit 1 | Orbit 2 |
|----|---------|---------|---------|
| \(\tau_1\) | 1 | \((A,0,0)\) | \((0,0,0)\) | \((2C,C,0)\) |
|     | 2 | \((0,B,0)\) | \((0,B,0)\) | \((0,-B,0)\) |
| \(\tau_3\) | 1 | \((A,0,0)\) | \((A,0,0)\) | \((-A,-A,0)\) | \((-A,-A,0)\) |
|     | 2 | \((0,B,0)\) | \((0,B,0)\) | \((0,B,0)\) | \((0,B,0)\) |
| \(\tau_5\) | 1 | \((0,0,A)\) | \((0,0,A)\) | \((0,0,A)\) | \((0,0,A)\) | \((0,0,C)\) | \((0,0,C)\) |
| \(\tau_7\) | 1 | \((0,0,A)\) | \((0,0,A)\) | \((0,0,-A)\) | \((0,0,-A)\) |

The active IR-s common for Pd displacements and quadrupolar ordering are \( \tau_1, \tau_3, \tau_5 \) and \( \tau_7 \). Because these representations are real and one dimensional, the BV-s calculated by the MODY program give directly the possible displacements of Pd atoms leading to the structures with the symmetry groups discussed earlier for the quadrupolar ordering. They are listed in the Table 4a and 4b.
Table 4b. Possible displacements of Pd atoms at 6(g) sites for $k=(1/2,0,0)$ accompanying the quadrupolar ordering

| IR | Version | Orbit 1 | Orbit 2 |
|----|---------|---------|---------|
|    |         | Pd1     | Pd2     | Pd3     | Pd4     | Pd5     | Pd6     |
| $\tau_1$ | 1        | $(A,0,0)$ | $(A,0,0)$ | $(A,A,0)$ | $(A,A,0)$ |         |         |
|        | 2        | $(0,B,0)$ | $(0,B,0)$ | $(0,-B,0)$ | $(0,-B,0)$ |         |         |
|        | 3        | $(0,0,A)$ | $(0,0,-A)$ | $(0,0,A)$ | $(0,0,-A)$ |         |         |
| $\tau_3$ | 1        | $(A,0,0)$ | $(A,0,0)$ | $(-A,-A,0)$ | $(-A,-A,0)$ |         |         |
|        | 2        | $(0,B,0)$ | $(0,B,0)$ | $(0,B,0)$ | $(0,B,0)$ |         |         |
|        | 3        | $(0,0,A)$ | $(0,0,-A)$ | $(0,0,A)$ | $(0,0,-A)$ |         |         |
| $\tau_5$ | 1        | $(A,0,0)$ | $(-A,0,0)$ | $(A,A,0)$ | $(-A,-A,0)$ |         |         |
|        | 2        | $(0,B,0)$ | $(0,-B,0)$ | $(0,-B,0)$ | $(0,B,0)$ |         |         |
|        | 3        | $(0,0,A)$ | $(0,0,A)$ | $(0,0,A)$ | $(0,0,A)$ |         |         |
| $\tau_7$ | 1        | $(A,0,0)$ | $(-A,0,0)$ | $(-A,-A,0)$ | $(A,A,0)$ |         |         |
|        | 2        | $(0,B,0)$ | $(0,-B,0)$ | $(0,B,0)$ | $(0,-B,0)$ |         |         |
|        | 3        | $(0,0,A)$ | $(0,0,-A)$ | $(0,0,A)$ | $(0,0,-A)$ |         |         |

Table 4c. Possible displacements of uranium atoms in 2(c) positions for $k=(1/2,0,0)$ accompanying quadrupolar ordering with active IR-s $\tau_1$, $\tau_3$ and $\tau_5$

| IR | U3 | U4 |
|----|----|----|
| $\tau_1$ | $(2A,A,0)$ | $(2A,A,0)$ |
| $\tau_2$ | $(0,A,0)$ | $(0,A,0)$ |
| $\tau_3$ | $(0,0,A)$ | $(0,0,A)$ |

6. Quadrupolar ordering and structural deformations in UPd$_3$

Below the first transition temperature $T_0=7.6$K the ordering of quadrupolar moments localised on U positions is found, with wave vector $k=(1/2,0,0)$. The quadrupolar moments at U1 and U2 sites form an antiquadrupolar arrangement, which is probably accompanied by structural deformations (atomic displacements) leading to orthorhombic symmetry. The principal axes of QMT are parallel to the orthorhombic system axes. The symmetry of the AFQ ordering mode can be described by the $(Q_{z^2,-r^2})$ type of quadrupolar operator at U(2a) sites. For $T_1 < T < T_0$ the experimental data are consistent with the model described by $\tau_5$, leading to the $P$ mnmm symmetry group, and the set of parameters given by $p=(Q;2Q;0,0,0)$ for U(2a) sites. Such quadrupolar ordering may be accompanied by displacements parallel to the z axis for Pd atoms at (6h) sites and parallel to the z axis or located in the basal plane for Pd atoms at (6g) sites (see Table 4a and Table 4b). Magnitudes and signs of displacements for atoms belonging to the first orbit are independent to the magnitudes and signs of displacements of the atoms belonging to the second orbit. Within each orbit in one hexagonal elementary cell the displacements...
are parallel. One of the possible models of common quadrupolar and structural ordering in this temperature range is shown in Figure 4.

![Diagram showing quadrupolar and structural ordering](image)

**Figure 4.** One of the possible models of common quadrupolar and structural ordering for IR $\tau_5$, quadrupolar parameter set $(Q, 2Q, 0, 0, 0)$ and independent amplitudes of atomic displacements for various orbits of Pd atoms.

Below $T_1 = 6.9$K and $T_2 = 6.7$K temperatures further deviations of the QMT principal axes directions are observed, leading to further symmetry reductions of AFQ ordering at U(2a) sites, which are respectively described by $\left(Q_{x2}, Q_{y2}\right)$ and $\left(Q_{x2}, Q_{y2}, Q_{z2}\right)$ quadrupolar operators. It corresponds to the symmetry analysis result described by the $\tau_3$ IR, with the set of parameters given by $p = (0, B, 0, B)$. The addition of emergence of $\tau_3$ solution leads to the rotation of the $\tau_5$ QMT shape along the orthorhombic $x$ axis (Q1 and Q2 in antiphase) and change of the QMT shape. Next the $\tau_1$ solution is added, with the set of parameters given by $p = (0, 0, Q', Q', 0)$, leading to the rotation of the $\tau_5$ QMT shape along the $y$ axis (Q1 and Q2 also in antiphase) and further change of the QMT shape. Such quadrupolar ordering may be also accompanied by additional displacements of Pd atoms in the basal plane at (6h) and (6g) sites, which are given in the Table 4a and 4b. Below $T_1$ the possible $\left(Q_{z2}\right)$ deviations at U(2c) sites [2] correspond to the $\tau_5$ IR and parameter set $p' = (C', C')$. The resulting type of structure belongs to the monoclinic symmetry. The last stage described above (for $T < T_1$) is probably not a valid description of the situation in UPd$_3$ as the experimental data [6] strongly indicate, that a triple-q phase is formed below $T_1$ temperature in a discontinuous phase transition. The symmetry analysis of the triple-q phase with corresponding quadrupolar, structural and magnetic ordering will be discussed in the next paper.
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