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MODY – calculation of ordered structures by symmetry-adapted functions

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Abstract: In this paper we focus on the new version of computer program MODY for calculations of symmetry-adapted functions based on the theory of groups and representations. The choice of such a functional frame of coordinates for description of ordered structures leads to a minimal number of parameters which must be used for presentation of such structures and investigations of their properties. The aim of this work is to find those parameters, which are coefficients of a linear combination of calculated functions, leading to construction of different types of structure ordering with a given symmetry. A spreadsheet script for simplification of this work has been created and attached to the program.

Keywords: ordered structures; symmetry analysis; theory of groups and representations; computer program

PACS: 60; 61.50.Ah; 61.43.Bn; 61.50.Ks

1 Theoretical introduction

When a complex system (physical, biological, social or numerical) in some conditions becomes ordered, the knowledge of its symmetry leads to a significant simplification of the description of such a system as well as the investigation of its properties. The most suitable mathematical tools for studying symmetry are those developed by the theory of groups and their representations. The set of transformations which leave the system invariant forms its symmetry group. Transformation rules for functions describing the properties of the system, defined on the space with a given symmetry group, can be described in terms of the -representations of the group.

Theory of group representations was developed many years ago. E. Wigner [1] G.J. Lubarski [2] and A.P. Cracknell [3] introduced the set of basis vectors of irreducible representations for molecular symmetry groups in calculations of molecular vibrations as "symmetric coordinates". Later, this method was also used also for the analysis of different continuous, structural phase transitions (for example permutational, displacive, magnetic or quadrupolar types). The examples of their works may be found in [4–14]. Continuous (or semi-continuous) phase transitions, for example, in crystals, occur when under certain circumstances occur (e.g. change of temperature, external pressure or magnetic field) in the parent structure with the highest symmetry. This leads to changes taking place, leading to lower crystal symmetry with preservation of the group-subgroup relation. Because of strong restrictions imposed by symmetry of the space where the phase transition takes place, not all changes are permitted. The symmetry analysis method based on the representations of parent symmetry group is able to predict all possible channels of structural transformations and indicate the forbidden ones.

A typical situation in which the symmetry analysis is applied to the description of the ordering process in solids mentioned above includes the following features:

- There is a well defined high-symmetry (high-temperature) phase, with a well-known symmetry space group and with well known sets of e quivalent positions (Wyckoff positions) in the unit cell.
- A local physical quantity exists, with known rules of transformations under the action of operations belonging to crystal symmetry group, defined on one or more symmetry equivalent sets of sites in the unit cell, which becomes non-zero in the low-symmetry phase, thus representing a deviation from the high-symmetry state of the crystal.
- There is a wave vector (given in reciprocal lattice) responsible for the ordering process, usually known from the experiment, which describes the propagation direction and wavelength of ordering waves,

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thus defining the relations between the values of the ordering quantity in neighboring unit cells of the crystal. The modulus of the ordering wave vector k may be commensurate; leading to unit cell multiplication in the low-symmetry phase, or incommensurate; leading to an incommensurately modulated phase. The set of symmetry equivalent vectors k is denoted as $\{k_L\}$ and it is called the k-vector star. Each individual vector k in the set is called an arm of the star. The set of symmetry operations leaving the vector k unchanged is called the k-vector symmetry group $G(k)$.

In such circumstances every physical quantity of the crystal that is localized on the atom sites may be described by a Wannier function S, defined on a set of equivalent positions. It may be a scalar (the change of site occupation probability), a polar vector (displacements of atoms from the equilibrium positions), an axial vector (the ordering of magnetic moments) or even a tensor (the ordering of quadrupole moments).

$$\overrightarrow{S} = \begin{bmatrix} \begin{bmatrix} \hat{u}(\vec{r}_1) \\ \hat{u}(\vec{r}_2) \\ \hat{u}(\vec{r}_3) \\ \vdots \\ \hat{u}(\vec{r}_n) \end{bmatrix} \\ \vdots \\ \begin{bmatrix} \hat{u}(\vec{r}_1 + \vec{t}_{p,q,s}) \\ \hat{u}(\vec{r}_2 + \vec{t}_{p,q,s}) \\ \hat{u}(\vec{r}_3 + \vec{t}_{p,q,s}) \\ \vdots \\ \hat{u}(\vec{r}_n + \vec{t}_{p,q,s}) \end{bmatrix} \end{bmatrix}, \qquad \vec{t}_{p,q,s} = p\vec{a}_1 + p\vec{a}_2 + p\vec{a}_3$$

where a_1, a_2, a_3 are the respective lattice constants of the periodic structure, and p, q, s are integers.

As may be seen from the equation above the presentation of the function S in the commonly used coordinate frame related to the crystallographic system, $u = (u_x, u_y, u_z)$, which takes advantage of the translation symmetry and reduces the number of parameters needed for the description of the elementary cell. The other symmetry relations are lost in this description. As a consequence, the space of unknown parameters (SUP) is multi-dimensional and the description of many crystal properties becomes unnecessarily complicated.

According to the law proved by Wigner [1] each function defined in the space with a given symmetry group may be presented as linear combination of the so called basis vectors (BVs) of the irreducible representations of this symmetry group (IRs). Thus, the Wannier function is expressed as a linear combination of the BVs:

$$\vec{S}^{\{k_L\}} = \sum_{k_L} \sum_{\nu=1}^{j} \sum_{\lambda=1}^{l_\nu} C_{\nu,\lambda}^{(k_L)} \vec{\Psi}_{\nu,\lambda}^{(k_L)}$$

$$= \sum_{k_L,\nu,\lambda} C_{\nu,\lambda}^{(k_L)} \begin{bmatrix} \begin{bmatrix} \hat{\Psi}_{\nu,\lambda}^{(k_L)}(\vec{r}_1) \\ \hat{\Psi}_{\nu,\lambda}^{(k_L)}(\vec{r}_2) \\ \vdots \\ \hat{\Psi}_{\nu,\lambda}^{(k_L)}(\vec{r}_n) \end{bmatrix} \\ \vdots \\ \begin{bmatrix} \hat{\Psi}_{\nu,\lambda}^{(k_L)}(\vec{r}_1) e^{i\vec{k}_L\vec{t}} \\ \hat{\Psi}_{\nu,\lambda}^{(k_L)}(\vec{r}_2) e^{i\vec{k}_L\vec{t}} \\ \vdots \\ \hat{\Psi}_{\nu,\lambda}^{(k_L)}(\vec{r}_n) e^{i\vec{k}_L\vec{t}} \end{bmatrix} \end{bmatrix}$$

where $\vec{\Psi}_{\nu,\lambda}^{(k_L)}$ are the BVs and the indices k_L, ν, and λ correspond, to the vectors k, the number of the respective IR of the group, and the dimensions of the respective IR, respectively.

The BVs are calculated within the frame of group theory and are well known in the discussion of phase transitions. Details of the procedure used in the presented program can be found in [7]. The unknown parameters leading to different types of possible ordering structures after the phase transition is represented as $C_{\nu,\lambda}^{(k_l)}$. The most probable case is the phase transition occurring according to one of the IRs and one k-vector, (the new structure is realized within one of the irreducible subspaces of IR, on which the SUP splits), so number of unknown parameters needed for the presentation of S function in BV functional frame of coordinates depends only on the dimension of the respective IR.

As it may be seen, the presentation of the model structure in the terms of the basis vectors, $C_{\nu,\lambda}^{(k_l)}$, leads to simplest description of the structure than the frame of the crystallographic system (x, y, z). This kind of description better reflects the symmetry of the problem and requires the lowest number of independent parameters.

For calculations of BVs, except for the knowledge of the symmetry of positions; the knowledge of the rules of transformations of physical quantities, localized on these positions, under the symmetry operations is needed. The transformation matrices related to scalar, polar, and axial vectors used in the SA are standard. For the tensor case it requires further explanation.

The electric potential from any charge distribution may be written as a sum of monopolar, dipolar, quadrupolar, and higher contributions. In the presented analysis, it is assumed that the dipole potential and higher order moments are absent and therefore the initial form of the total

potential exhibits spherical symmetry. The components of 3×3 quadrupole moment tensor (QMT) are usually defined as volume integrals of charge density with respective coordinate combinations [16]. The component values uniquely define the orientational distribution of the quadrupolar potential. In general, the QMT matrix has nine components, but taking into account that it is symmetrical and traceless, only five components are independent. For the convenient application of symmetry analysis, the components of quadrupole moment tensor are rearranged into a vector form, as shown in following equation.

$$\hat{Q}_{gen} = \begin{pmatrix} Q_{11} & Q_{12} & Q_{13} \\ Q_{12} & Q_{22} & Q_{23} \\ Q_{13} & Q_{23} & (-Q_{11} - Q_{22}) \end{pmatrix}$$

$$\hat{u}(\vec{r}_n) = \begin{bmatrix} u_{11} & u_{12} & u_{13} \\ u_{21} & u_{22} & u_{23} \\ u_{31} & u_{32} & u_{33} \end{bmatrix} \Rightarrow \begin{bmatrix} u_{11}(\vec{r}_n) \\ u_{12}(\vec{r}_n) \\ u_{13}(\vec{r}_n) \\ u_{21}(\vec{r}_n) \\ u_{22}(\vec{r}_n) \\ u_{23}(\vec{r}_n) \\ u_{31}(\vec{r}_n) \\ u_{32}(\vec{r}_n) \\ u_{33}(\vec{r}_n) \end{bmatrix}$$

The requirements imposed on the symmetry-adapted solution for physical quantities represented by tensors include the reality condition analyzed in the section discussing vectors, but additionally there are the conditions imposed by the internal features of QMT. These type of conditions are specific for a given physical quantity represented by the tensor, and for e.g. the moment of inertia, the zero trace condition would be absent. Thus, the conditions are of physical origin, like the "constant moment" conditions for magnetic ordering modes. In practice, these extra requirements eliminate some of the solutions obtained from symmetry analysis that conform to the reality requirement. Another criterion that can be used for selection of the final solution is the direct relation between the quadrupolar transition and the accompanying structural changes. It is possible to calculate the atomic displacements for a given IR, and then to calculate the final symmetry group. When the final symmetry group is known from the experiment, the number of possible IRs that are active in the transition is drastically reduced. In the next step, one can calculate the details of the quadrupolar transition for the same symmetry changes even if the experimental data on the quadrupolar transition are far from being complete.

2 MODY – computer program for calculation of BVs

The MODY program has been developed since the 1990s. It performs most calculations related to the theory of groups and representations, especially the BVs of IRs.

The previous version of MODY program was described in the quoted literature [8, 15]. New version of the program has obtained a new, more compact form. It was written in C++ in CodeBlocks framework with wxWidgets library. All input and output settings (parameters) were placed in one window.

The input part is placed on the left side of the main program window. There are following sections in this part:

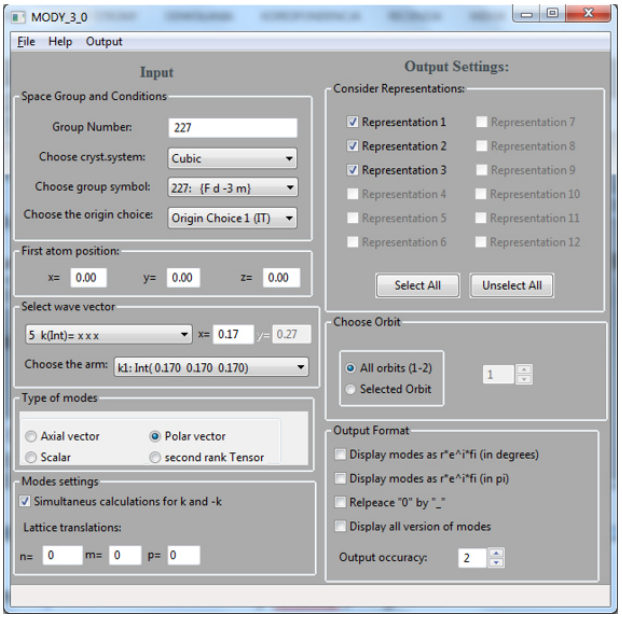


Figure 1: The main window of the new version of MODY program.

- Space group and Conditions – allows typing in or choice of space group according to International Crystallographic Tables notation. You can also select the origin choice, if the Crystallographic Tables contain more than one.
- First atom position - allows the specification of the first atom coordinates according to International Crystallographic Tables notation.
- Select wave vector - allows selection of the wave vector. The pull-down list contains all (nonequivalent) wave vectors allowed for given group. For incommensurate vectors the wave vector components con-

tain parameters x, y. In the calculations their actual values are used, which can be typed in the edition fields "x=" and "y=". The default value of these parameters are set as nonzero values equal to 0.17 and 0.27 respectively. The values of x and y parameters do not affect the mode type (their symmetry), they merely specify their absolute values. This section allows also the selection of the arm of wave vector star k in the conventional reciprocal lattice coordinate system. All arms of the selected k-vector star are calculated for given group and are available on the list of combo box.

- Type of modes - that group of options allows the selection of the mode type out of four types of physical quantities: scalar, polar vector, axial vector or second rank Tensor.
- Modes settings – Checking of the selection field "Simultaneous calculations for k and $-k$" results in the calculation and presentation of mode values for both wave vectors: k and $-k$. "Lattice translations" text fields group allows the specification of lattice translations e.g. selection of the conventional unit cell for which the modes will be calculated by specifying the shift from "zero unit cell" by a vector $\vec{t} = \vec{n}\vec{a} + m\vec{b} + p\vec{c}$, where $\vec{a}$, b, $\vec{c}$ are conventional lattice basic vectors. For the n,m,p coefficients only integer values are accepted.

The output part is placed on the right side of program window. There are following sections in this part:

- Consider Representations - allows selection of the representations for which calculations of modes will be made. Only active representations are enabled for selection.
- Choose orbit – allows the choice of orbit of sites for calculation of modes.
- Output format – allows the selection of modes format for output.
- Modes can be displayed in following forms: as $C(\cos\phi + i^*\sin\phi)$ (default), as $re^{i\phi}$ ($r\phi[°]$) and as $re^{i\phi}$ ($r\phi[\pi\ units]$).
- Switching the "Display 0 by _" option on results in replacement of the zero digits in the output report by the underscore character.
- Switching "Display all mode versions" options on results in listing of all the modes, including the zero amplitude modes and equivalent modes. Switching this option off results in application of a mode reduction procedure and only the non-zero and essentially non-equivalent modes are listed.
- Output accuracy allows the setting of output accuracy (the number of digital places) for presentation of the output data

All important output reports were also placed in one menu. The format of output data is completely determined by the settings of output part in the main program window.

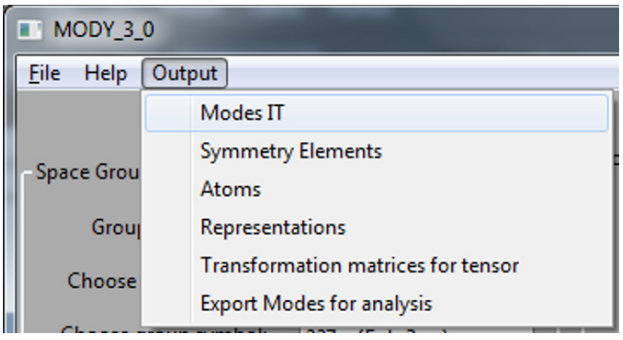


Figure 2: Output reports of the MODY program.

The new version of MODY program delivers the following output reports:

- Modes IT - modes are calculated and presented in the conventional IT setting for the irreducible representations and *G(k1)* orbits selected in the input section.
- Symmetry Elements - presents the information on symmetry elements of the full space group *G*and the wave vector group *G(k1)*.
- Atoms - presents the report on atomic positions. All atomic positions are generated by action of matrices of symmetry elements on the position vector of the first atom.
- Representations - presents the report on symmetry elements representations in the Kovalev set.
- Transformation matrices for tensors - shows the default tensor transformation matrices for individual symmetry elements of the space group. The matrices are available only for the "Second rank Tensor" mode type. The matrices are constructed as R x R(direct product), where R is the transformation matrix (3x3) for a given symmetry element.
- Export Modes for analysis - show modes (like Modes IT output) in special form dedicated for import in excel spreadsheets, which may be used for searching of fitting coefficients.

As shown in [14] the calculation of coefficients for linear combination of basis vectors in an analytical form is com-

plex and difficult to implement. In practice, the fitting process is achieved by guessing and verifying the guessed coefficients. The experience of the person, who controls the procedure plays an important role in this process.

Two spreadsheet files were attached to the MODY program as tools for finding the coefficients of fitted structure. One of the spreadsheets is dedicated to finding the coefficients of vector modes (axial and polar), the second one for second rank tensor modes.

Figure 3: The spreadsheet for finding the linear combination coefficients for vector type quantities.

A linear combination of modes is carried out most likely for one representation, one orbit and one arm of the star of the wave vector k (or jointly for k and minus k).

Each of the mode type is transformed according to the type of quantity that it represents. Linear combination of modes represents the physical quantity of a given type (mode type) when it gives real values in all positions of orbit atoms. Thus, only some of the coefficient sets in the linear combination of modes lead the real values in the atom positions thus representing the physical quantity of a given type e.g. site occupation probability, atomic displacements, magnetic moments or quadrupole moment.

3 Searching of the fitting coefficients (SFC-method)

As mentioned before the most probable transitions are usually going according to one IR and one k-vector (or k and minus k). Thus, only such cases may be analyzed in the attached spreadsheets. Therefore, after calculation of modes in MODY program, only one representation and one orbit of G_k must be selected for output. The calculated modes should be shown and saved to a text file with "Export Modes for analysis" menu command. The spreadsheet can properly read only files obtained in this way. This file should be opened in the "data" sheet. The spreadsheet analyzes this data and uses it to fill in the other sheets. Fitting coefficients should to be looked for in the sheet called "Adjustment_Atom1". The form in this sheet contains all modes for the first atom, which was imported to data sheet from the text file. Next to each mode the coefficient C_i set as r_c, ϕ_c. (i.e. $r_c e^{\phi c}$) is placed. The value of each coefficient can be changed using the controls. The linear combination of all modes with current values of coefficients can be seen in the top part of the sheet as values and charts, separately for each component x, y, z.

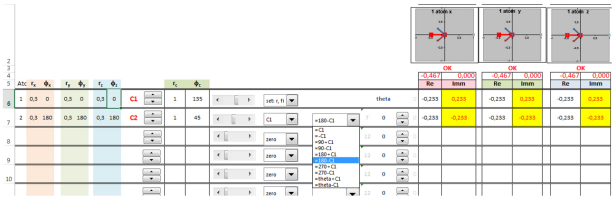


Figure 4: Setting the relations between coefficients.

Charts present the values of coefficients of analyzed quantity on the complex plane. So only values of linear combination located on the horizontal line correspond to a real value and are allowed as physical results. The real and imaginary components for the linear combination result are shown under the chart. The imaginary component of the result has to be zero to represent a physical quantity.

In one chart every mode multiplied by its coefficient is shown separately (in black) and additionally the resulting linear combination is shown (in red) for a given component.

Charts are updated on an ongoing basis so changes resulting from setting the coefficients can be observed. Dynamic tracking of the results of the linear combination can indicate the desired direction of the coefficient corrections.

Coefficient can be set independently of each other ("set r, fi" option in first combo box) or take zero value ("zero" option). Very often some subsets of coefficients combined affect only one component. The form in this sheet gives possibility to connect a change of the current coefficient with the previous one ("C1" options). In such cases the specific relation between coefficients can be set by the second combo box.

Some typical relations between phases of coefficients may by chosen as: *Cj=±Ci*, *Cj=90°±Ci*, *Cj=90°±Ci*, *Cj=270°±Ci*, *Cj=theta°±Ci* where *i<j*. The last case allows to set other value of phase difference for relation between coefficients (it may be set next to this combo box).

Obtaining the real values of the linear combination of modes for the first atom is the essential condition. In addition to this getting real values of linear combination of modes is necessary for the rest of the atoms in orbit. This requirement may be checked in the following sheets. The "Other_Atoms" sheet presents values of modes, coeffi-

cients and combination and the "Atoms_Graph" sheet contain Charts for the rest of atoms.

The second spreadsheet is dedicated to finding the coefficient of linear combination for the second rank tensor modes. The way of searching is similar to the one used in the vector modes. In this case the number of dimension is higher and the number of complex values which should be analyzed grows from 3 to 9 for each atom.

4 Example of ordering analysis in TmTe

For illustration of the possibilities of SA and SFC-method the short discussion of the quadrupolar ordering and the related structural deformations in TmTe compound is given below (it is discussed in details in F. Bialas PhD dissertation [23]).

The TmTe compound crystallizes in the structure NaCl type described by *Fm-3m* (IT no 225) space group. It was shown that the presence of quadrupolar phase transition bellow, TQ = 1.8K, described by wave vector k =(1/2, 1/2, 1/2). The Tm atoms occupies 4(a) positions Tm1:(0, 0, 0), Tm2:(0, 1/2, 1/2), Tm3:(1/2, 0, 1/2), Tm4:(1/2, 1/2, 0). The Te atoms occupies 4(b) positions Te1:(1/2, 1/2, 1/2), Te2:(1/2, 0, 0), Te3:(0, 1/2, 0), Te4:(0, 0, 1/2). Numerous experimental and theoretical works describe the changes of properties of the compound in the phase transition [17–21]. Especially valuable is the theoretical work of Nikolaev [22]. The author has included in its paper the analysis of the symmetry used for the microscopic calculation in his paper. He gives obtained in this way quadrupolar ordering and accompanying structural displacements obtained in this way. It allows direct comparison of the results of the symmetry produced by the method presented in this study with the results obtained by another method.

4.1 Quadrupolar ordering on Tm atoms

The calculations made with the program MODY indicate that the quadrupolar ordering described by the wave vector k =(1/2,1/2,1/2) and for position 4(a) are allowed to be active in the phase transition only representations τ_1, τ_3, and τ_5. The linear combination of BV $\sum_i c_i \Psi_{\vec{k},\tau_v,i}$ has set the form of TMK e.g. the matrix has to be symmetric, traceless and has the real coefficients for every representation.

Matrices of BV for τ_3 representation are antisymmetric, 1-dimentional and occurring one time. Because of that they may not represent quadrupolar tensor matrices.

Representation τ_1

One-dimensional representation τ_1 occurs two times in the decomposition, thus two coefficients of the linear combination should be considered for the construction of final QMT. Modes calculated for this representation, 4(a) site and wave vector k =(1/2 , 1/2, 1/2) have the following form.

	BVof IR	Tm1	Tm2, Tm3, Tm4
version 1	$\Psi_{k,\tau_1,1}$	$\begin{bmatrix} 0{,}33 & 0 & 0 \\ 0 & 0{,}33 & 0 \\ 0 & 0 & 0{,}33 \end{bmatrix}$	$\begin{bmatrix} -0{,}33 & 0 & 0 \\ 0 & -0{,}33 & 0 \\ 0 & 0 & -0{,}33 \end{bmatrix}$
version 2	$\Psi'_{k,\tau_1,1}$	$\begin{bmatrix} 0 & 0{,}17 & 0{,}17 \\ 0{,}17 & 0 & 0{,}17 \\ 0{,}17 & 0{,}17 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & -0{,}17 & -0{,}17 \\ -0{,}17 & 0 & -0{,}17 \\ -0{,}17 & -0{,}17 & 0 \end{bmatrix}$

Figure 5: Modes for IR τ_1, 4(a) sides and wave vector k=(1/2, 1/2, 1/2).

It is impossible to obtain a matrix with properties of QMT from elements of the first version because the trace of the matrices are non-zero. The second version provides with any real parameter c directly QMT matrices as shown in the following table.

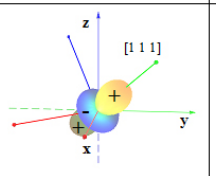
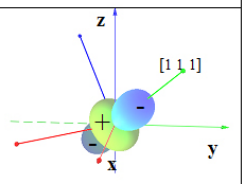
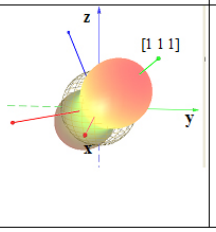
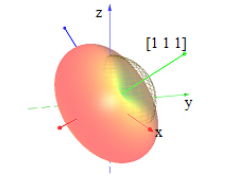
	Tm 1	Tm2, Tm3, Tm4
QMT matrix	$c\begin{bmatrix} 0 & 0{,}17 & 0{,}17 \\ 0{,}17 & 0 & 0{,}17 \\ 0{,}17 & 0{,}17 & 0 \end{bmatrix}$	$c\begin{bmatrix} 0 & -0{,}17 & -0{,}17 \\ -0{,}17 & 0 & -0{,}17 \\ -0{,}17 & -0{,}17 & 0 \end{bmatrix}$
directional quadrupolar potential distribution		
directional total potential distribution		

Figure 6: Quadrupolar ordering according to representation τ_1, 4(a) sites and k=(1/2, 1/2, 1/2).

The quadrupole moments at atom side position Tm1 at the rest positions (Tm2, Tm3, Tm4) have the same directions of main axes but correspond to opposite deformation of potential. The ordered structure has symmetry of wave vector group G_k : *R-3m* (IT nr 166) and a specific free rotation axis [1, 1, 1] lies along to threefold symmetry axis of destination group. Because of k =(1/2, 1/2, 1/2), coefficients of QTM for 4(a) site in the next elementary cell in every axes have opposite signs. It corresponds to opposite deformation of potential.

Representation τ_5

Two-dimensional representation τ_5 occur three times in the decomposition, thus six coefficients of the linear combination should be considered for the construction of final QMT. Modes calculated for this representation, 4(b) site and wave vector k=(1/2, 1/2, 1/2) are shown in the following table.

	Coefficient	mode	Tm1	Tm2, Tm3, Tm4
version 1	C_1	$\Psi_{\vec{k},\tau_5,1}$	$0.17\begin{bmatrix}1&0&0\\0&e^{i\frac{2}{3}\pi}&0\\0&0&e^{-i\frac{2}{3}\pi}\end{bmatrix}$	$0.17\begin{bmatrix}-1&0&0\\0&e^{-i\frac{1}{3}\pi}&0\\0&0&e^{i\frac{1}{3}\pi}\end{bmatrix}$
	C_2	$\Psi_{\vec{k},\tau_5,2}$	$0.17\begin{bmatrix}e^{i\frac{2}{3}\pi}&0&0\\0&1&0\\0&0&e^{-i\frac{2}{3}\pi}\end{bmatrix}$	$0.17\begin{bmatrix}e^{-i\frac{1}{3}\pi}&0&0\\0&-1&0\\0&0&e^{i\frac{1}{3}\pi}\end{bmatrix}$
version 2	C_1'	$\Psi'_{\vec{k},\tau_5,1}$	$0.17\begin{bmatrix}0&1&0\\0&0&e^{i\frac{2}{3}\pi}\\e^{-i\frac{2}{3}\pi}&0&0\end{bmatrix}$	$0.17\begin{bmatrix}0&-1&0\\0&0&e^{-i\frac{1}{3}\pi}\\e^{i\frac{1}{3}\pi}&0&0\end{bmatrix}$
	C_2'	$\Psi'_{\vec{k},\tau_5,2}$	$0.17\begin{bmatrix}0&0&e^{i\frac{2}{3}\pi}\\1&0&0\\0&e^{-i\frac{2}{3}\pi}&0\end{bmatrix}$	$0.17\begin{bmatrix}0&0&e^{-i\frac{1}{3}\pi}\\-1&0&0\\0&e^{i\frac{1}{3}\pi}&0\end{bmatrix}$
version 3	C_1''	$\Psi''_{\vec{k},\tau_5,1}$	$0.17\begin{bmatrix}0&0&1\\e^{i\frac{2}{3}\pi}&0&0\\0&e^{-i\frac{2}{3}\pi}&0\end{bmatrix}$	$0.17\begin{bmatrix}0&0&-1\\e^{-i\frac{1}{3}\pi}&0&0\\0&e^{i\frac{1}{3}\pi}&0\end{bmatrix}$
	C_2''	$\Psi''_{\vec{k},\tau_5,2}$	$0.17\begin{bmatrix}0&e^{i\frac{2}{3}\pi}&0\\0&0&1\\e^{-i\frac{2}{3}\pi}&0&0\end{bmatrix}$	$0.17\begin{bmatrix}0&e^{-i\frac{1}{3}\pi}&0\\0&0&-1\\e^{i\frac{1}{3}\pi}&0&0\end{bmatrix}$

Figure 7: Modes for IR τ_5, 4(a) sides and wave vector k=(1/2, 1/2, 1/2).

Only the first version of BVs has non zero elements on diagonal in QTM matrices thus coefficients corresponded to them may be considered separately. The spreadsheet for finding the coefficients of linear combination for the second rank tensor modes allows various values of coefficients. By changing the coefficients c_1 and c_2 (for modes of version 1) specific forms of the final matrix which satisfy the conditions of the QMT matrix can be easily obtained. But very often the coefficients are connected with each other. In this case, the family of solutions is obtained. The form of connected coefficients can be guessed from particular solutions or obtained by testing various relations between coefficients in spreadsheet.

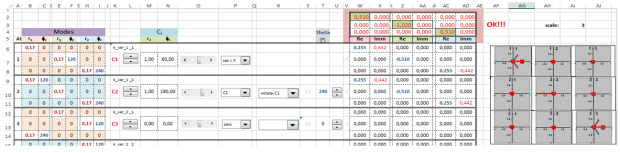


Figure 8: Finding the linear combination of TmTe compound, for quadrupolar ordering, representation τ_5, and coefficients (5).

It is simply to check that the set of coefficients *c*

$$c_1 = ce^{i\phi},\ c_2 = ce^{i(\frac{4}{3}\pi-\phi)};\ c_1' = 0,\ c_2' = 0;\ c_1'' = 0,\ c_2'' = 0;$$

witch correspond to modes of version 1 only, gives the following form of QMTs

	QMT
Tm1	$c\begin{bmatrix}2\cos\varphi&0&0\\0&2\cos(\frac{2}{3}\pi+\varphi)&0\\0&0&2\cos(\frac{2}{3}\pi-\varphi)\end{bmatrix}$
Tm2, Tm3, Tm4	$c\begin{bmatrix}-2\cos\varphi&0&0\\0&-2\cos(\frac{2}{3}\pi+\varphi)&0\\0&0&-2\cos(\frac{2}{3}\pi-\varphi)\end{bmatrix}$

Figure 9: Matrices of the QMT for IR τ_5, 4(a) sites, wave vector k=(1/2, 1/2, 1/2) and coefficients (5); where ϕ - free parameter.

Any value of the free parameter, ϕ, leads to the form of QTM with three different main axes along to crystallographic axes. For some special values of free parameters, ϕ, the particular cases of symmetry QMTs are obtained. Such special cases are shown in the following table. For

the free parameter $\phi' = \phi + \pi$ the QMT matrix has opposite signs for all elements and the directional quadrupolar potential distribution and directional total potential distribution are opposite to those correspond to ϕ. For representation of τ_5 and any value of ϕ correspond to the order parameter $p_1 = (c_1, c_2)$ only identity-operation and inversion leave this order parameter unchanged. The final structure in this case has symmetry of space group *P-1* (IT no 2). The specular cases of quadrupolar symmetry structure occur for $\phi = \pi/6$ with order parameter $p_2 = (c, -c)$, and for $\phi = 2\pi/3$ with order parameter $p_3 = (c, c)$. In those cases two additional symmetry elements occur: twofold axis in [1, −1, 0] direction and symmetry plane described by Miller index (1, −1, 0). The crystal has after phase transition quadrupolar structure described by symmetry space group *C2/c* (IT no 15) or *C2/m* (IT no 12) respectively.

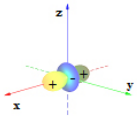
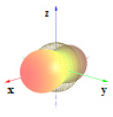
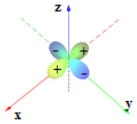
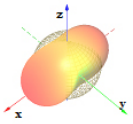
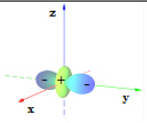
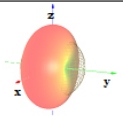
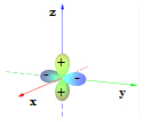
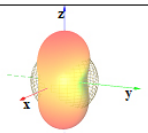
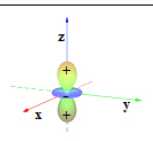
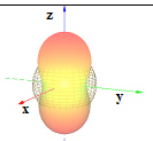
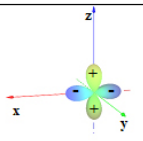
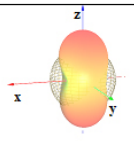
φ	Tm1		
[°]	QMT matrix	directional quadrupolar potential distribution	directional total potential distribution
0	$\begin{bmatrix} 2c & 0 & 0 \\ 0 & -c & 0 \\ 0 & 0 & -c \end{bmatrix}$		
30	$\begin{bmatrix} a & 0 & 0 \\ 0 & -a & 0 \\ 0 & 0 & 0 \end{bmatrix}$		
60	$\begin{bmatrix} c & 0 & 0 \\ 0 & -2c & 0 \\ 0 & 0 & c \end{bmatrix}$		
90	$\begin{bmatrix} 0 & 0 & 0 \\ 0 & -a & 0 \\ 0 & 0 & a \end{bmatrix}$		
120	$\begin{bmatrix} -c & 0 & 0 \\ 0 & -c & 0 \\ 0 & 0 & 2c \end{bmatrix}$		
150	$\begin{bmatrix} -a & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & a \end{bmatrix}$		

Figure 10: Quadrupolar ordering according to representation τ_5, 4(a) sites, k=(1/2, 1/2, 1/2), coefficient (5) and chosen values of free parameters $a = c\sqrt{3}$.

The remaining versions of modes (2 and 3) have matrices with non-zero complex elements outside of the diagonal. Four coefficients for those modes should be considered for the construction of the final matrix which satisfy the conditions of QTM.

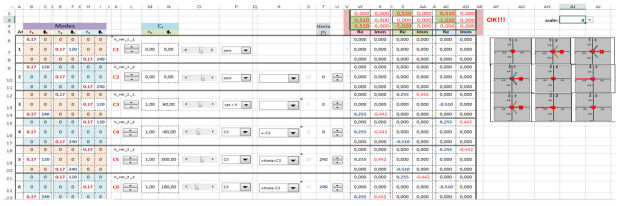


Figure 11: Finding the linear combination of TmTe compound, for quadrupolar ordering, representation τ_5, and coefficients (6).

As it can be seen, modes for coefficients c_1' (c_3 in spreadsheet) with c_2"(c_6) and c_2'(c_4) with c_1'(c_5) could be combined together because they affect the same elements of matrix. For correlation of $c_1' = ce^{i\phi}$, $c_2'' = ce^{i(\frac{4}{3}\pi-\phi)}$, and $c_2' = ce^{i\alpha}$; $c_1'' = ce^{i(\frac{4}{3}\pi-\alpha)}$ where φ, α- free phase, all elements of final matrix are real. But for any value of phases φ, α the final matrix is not symmetric. Only relations between all coefficients leads to symmetric matrix and satisfy the condition of QMT. In this case the set of coefficients

$$c_1 = 0,\ c_2 = 0;\ c_1' = ce^{i\phi}, c_2' = ce^{-i\phi};$$
$$c_1'' = ce^{i(\frac{4}{3}\pi+\phi)}, c_2'' = ce^{i(\frac{4}{3}\pi-\phi)}$$

leads to the following form of QMT matrix

	QMT
Tm1	$c\begin{bmatrix} 0 & 2\cos(\varphi) & 2\cos(\frac{2}{3}\pi-\varphi) \\ 2\cos(\varphi) & 0 & 2\cos(\frac{2}{3}\pi+\varphi) \\ 2\cos(\frac{2}{3}\pi-\varphi) & 2\cos(\frac{2}{3}\pi+\varphi) & 0 \end{bmatrix}$
Tm2, Tm3, Tm4	$c\begin{bmatrix} 0 & -2\cos(\varphi) & -2\cos(\frac{2}{3}\pi-\varphi) \\ -2\cos(\varphi) & 0 & -2\cos(\frac{2}{3}\pi+\varphi) \\ -2\cos(\frac{2}{3}\pi-\varphi) & -2\cos(\frac{2}{3}\pi+\varphi) & 0 \end{bmatrix}$

Figure 12: Matrix of the QMT for IR τ_5, 4(a) sites, wave vector k=(1/2, 1/2, 1/2) and coefficients (6); ϕ - free parameters.

Any value of parameter ϕ gives the QMT matrix with three different main axes of symmetry twice axes. Their directions depend on the values of coefficient ϕ. For the

spectacular values of parameter ϕ it obtains cases with particular symmetry as can be seen in the following table

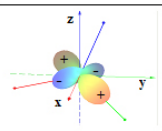
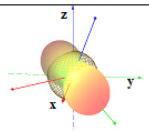
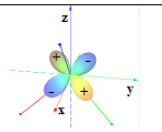
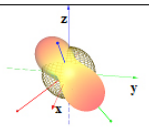
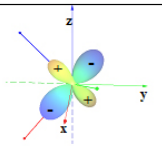
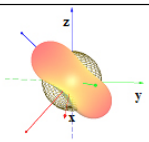
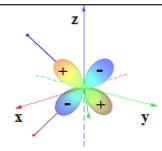
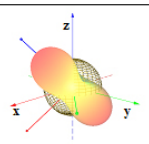
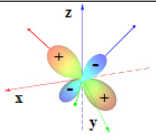
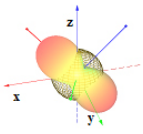
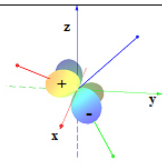
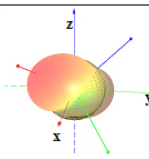
φ [°]	Tm 1 QMT matrix	directional quadrupolar potential distribution	directional total potential distribution
0	$\begin{bmatrix} 0 & 2c & -c \\ 2c & 0 & -c \\ -c & -c & 0 \end{bmatrix}$		
30	$\begin{bmatrix} 0 & a & 0 \\ a & 0 & -a \\ 0 & -a & 0 \end{bmatrix}$		
60	$\begin{bmatrix} 0 & c & c \\ c & 0 & -2c \\ c & -2c & 0 \end{bmatrix}$		
90	$\begin{bmatrix} 0 & 0 & a \\ 0 & 0 & -a \\ a & -a & 0 \end{bmatrix}$		
120	$\begin{bmatrix} 0 & -c & 2c \\ -c & 0 & -c \\ 2c & -c & 0 \end{bmatrix}$		
150	$\begin{bmatrix} 0 & -a & a \\ -a & 0 & 0 \\ a & 0 & 0 \end{bmatrix}$		

Figure 13: Quadrupolar ordering according to representation τ_5, 4(a) sites, k=(1/2, 1/2, 1/2) for coefficients (6) and parameter ϕ, $a = c\sqrt{3}$.

For the free parameter $\phi' = \phi + \pi$ the QMT matrix has opposite signs for all elements and the directional quadrupolar potential distribution and directional total potential distribution are opposite to those corresponding to the ϕ. Similarly to the fitting for the first modes version, the final structure has in general case symmetry of space group *P-1* (IT no 2). Two particular symmetry cases occur for ϕ =0 which correspond to free parameter

$$p_{2,3} = \left(c,\ c;\ ce^{i(\frac{4}{3}\pi)},\ ce^{i(\frac{4}{3}\pi)}\right),$$

and leads to the structure of space group *C2/m* and for $\phi = \pi/2$ which correspond to free parameter

$$p_{2,3} = \left(ic,\ -ic;\ ce^{i(\frac{11}{12}\pi)},\ -ce^{i(\frac{11}{12}\pi)}\right),$$

and leads to the structure of space group *C2/c*.

4.2 Possible associated structural changes

Possible structural changes for Tm atoms at 4(a) positions

The calculations made using the "polar vector" option of program MODY show that for positions 4 (a) and k = (1/2, 1/2, 1/2), the two irreducible representations are allowed to be active in the phase transition: a one-dimensional representation τ_4 and two-dimensional τ_6. Both representations occur once in the decomposition. However, neither of these representations is active in the quadrupolar phase transition. From the point of view of symmetry, there is no structural displacement of Tm atoms associated to quadrupolar ordering.

Possible structural changes for Te atoms at 4(b) positions

For the structural changes in the positions 4 (b) two IRs are active, one-dimensional τ_1 and two-dimensional τ_5. IRs are present in decomposition. Both IRs occur one time in the decomposition. These representations are also active in the quadrupolar transition. It gives the opportunity to displace the Te atoms accompanying to the quadrupolar transition.

Representation τ_1:

Structural modes calculated for representation τ_1 and sites 4(b) are real thus any real coefficients of linear combination give direct values of atoms displacement as show in following table.

	Te1	Te2, Te3, Te4	final symmetry group
basis vector	(1, 1, 1)	(-1, -1, -1)	R−3m (IT 166)
atom displacement	(C, C, C)	(-C, - C, - C)	

Figure 14: Structural modes and displacements of Te atoms at 4(b) positions for any real value of free parameter C, IR τ_1 and k=(1/2, 1/2, 1/2,).

Displacements of tellurium atoms at 4(b) positions according to τ_1 representation leads to the structure of *R-3m* (IT 166) symmetry of wave vector group.

Representation τ_5:

Structural modes calculated for representation τ_5 and sites 4(b) are shown in following table.

basis vector	Te1	Te2, Te3, Te4
$\Psi_{\vec{k},\tau_5,1}$	$C(1, e^{i\frac{2}{3}\pi}, e^{-i\frac{2}{3}\pi})$	$C(-1, -e^{i\frac{2}{3}\pi}, -e^{-i\frac{2}{3}\pi})$
$\Psi_{\vec{k},\tau_5,2}$	$C(e^{i\frac{2}{3}\pi}, 1, e^{-i\frac{2}{3}\pi})$	$C(-e^{i\frac{2}{3}\pi}, -1, -e^{-i\frac{2}{3}\pi})$

Figure 15: Structural modes for 4(b), IR τ_5 and k=(1/2, 1/2, 1/2).

Because the basic vectors are complex, it is required to use complex values of coefficients to obtain real values of atomic displacements.

The condition of real value of linear combination of basis vectors leads to following form of coefficients.

$$C_1 = Ce^{i\varphi}, \; C_2 = Ce^{i(\frac{4}{3}\pi-\varphi)}$$

where C, φ – free parameters.

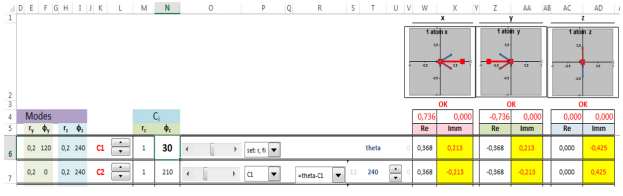


Figure 16: FFinding the linear combination of TmTe compound, for structural ordering, representation τ_5, and coefficients (9).

The values of atom displacements obtained for those coefficients were shown in the following table.

Atom	Displacement of atom
Te1	C(2cosϕ, 2cos(2/3π+ϕ), 2cos(2/3π-ϕ))
Te2, Te3, Te4	C(-2cosϕ, -2cos(2/3π+ϕ), 2cos(2/3π-ϕ))

Figure 17: Displacements of Te atoms at 4(b) positions, IR τ_5 and coefficients (9).

The final structure has in this case symmetry of space group *P-1* (IT no 2). For the free parameter $\phi' = \phi + \pi$ the atom displacements have opposite signs for all components relative to displacements corresponding to the ϕ. Particular cases symmetry occur for φ =0, φ = π/3, φ =2π/3 (then two components are equal *C*, the third coordinate is equal to *-2C*, and the final structure has symmetry of space group *C2/m*) and for φ = π/6, φ =3π/6, φ =5π/6 (then two components are equal to *C*, the third coordinate is equal *0*, and final structure has symmetry of space group *C2/c*).

Phase / coefficients	Atom displacement	
	Te1	Te2, Te3, Te4
ϕ=0	(2*C*, -*C*, -*C*)	(-2*C*, *C*, *C*)
ϕ=π/3	(*C*, -2*C*, *C*)	(-*C*, 2*C*, -*C*)
ϕ=2π/3	(-*C*, -*C*, 2*C*)	(*C*, *C*, -2*C*)
ϕ=π/6	(*C*, -*C*, 0)	(-*C*, *C*, 0)
ϕ=3π/6	(0, -*C*, C)	(0, *C*, -C)
ϕ=5π/6	(-*C*, 0, C)	(*C*, *0*, C)

Figure 18: Displacements of Te atoms at 4(b) positions, IR τ_5 and different values of the coefficients.

4.3 Summary

Symmetry analysis of TmTe allows ordering of quadrupole moments according to representations τ_1 and τ_5. None of these cases are accompanied by the displacement of atoms. Representation τ_1 leads to the ordering where the main axis of quadrupole moments lies along the [1, 1, 1] direction. Quadrupole moments at atom in (0, 0, 0) position has opposite form than at atoms at the center of faces. The final structure has symmetry of *R-3m* (IT no 166). Quadrupolar ordering according to representation τ_1 may be accompanied by displacement of Te atoms which respect symmetry of *R-3m* space group. Representation τ_5 gives possibility of various quadrupolar ordering. The first family of solutions with free parameter gives the orientation of the main axes of quadrupole moments along the crystallographic one. The second family of solutions also with free parameter, gives the orientation of the main axes of quadrupole moments along to any other directions. Any value of free parameter leads to the structure of low symmetry of space group *P-1* (IT no 2). For both the above families of solutions there exist particular values of free parameters, ϕ, which correspond to the order parameter of (c, c) and (c, -c) for which the final structures have respective symmetries of *C2/m* (IT no 12) or *C/2C* (IT no 15). The symmetry analysis permits this representation the occurrence of ordering associated displacements of atoms, which keep the symmetry of a quadrupolar structure. In the analysis of phase transition of TmTe delivered by Nikolaev and Michel [22] it used representation of group for cal-

culations of microscopic-energy. The results achieved in this way indicate that representation of τ_5 gives the ordering of symmetry of *C/2c* (IT no 15) or *C/2m* (IT no 12). The authors have not eventually settled which type of ordering occurs. Experimentally both these cases are equally likely.

References

[1] Wigner E., Nachr. Ges. Wiss. Gottingen 1930, 133.

[2] Lubarski G.J.,Teorija grupp i jejo prilozenije w fizikie, Moskwa, 1958 (in russion).

[3] Cracknell A.P., Applied Group Theory, Pergamon Press Ltd., 1968.

[4] Rado G.T., Suhl H., vol. 3, Chapt. 4, In: E.F. Bertaut (Ed.), Treatise on Magnetism, Academic Press, New York, 1963.

[5] Bertaut E.F., Magnetic structure analysis and group theory, J. Phys., 1971, 32 C1, 462-470.

[6] Izyumov Yu. A., Naish V. E., Ozerov R. P., Consultants Bureau, Neutron Diffraction of Magnetic Materials, A Division of Plenum Publishing Corporation, New York, 1991.

[7] Izyumov Yu.A., Syromyatnikov V.N., Phase Transitions and Crystal Symmetry, Kluwer Academic Publishers, Dordrecht, 1990.

[8] Sikora W., Białas F., Pytlik L., MODY: a program for calculation of symmetry-adapted functions for ordered structures in crystals, J. Appl. Cryst., 2004, 37, 1015-1019.

[9] Bilbao crystallographic server http://www.cryst.ehu.es.

[10] Capillas C., Kroumova E., Aroyo M.I., Perez-Mato J.M., Stokes H.T., Hatch D.M., SYMMODES: a software package for group-theoretical analysis of structural phase transitions, J. Appl. Cryst., 2003, 36, 953-954.

[11] Wills A.S., A new protocol for the determination of magnetic structures using simulated annealing and representational analysis (SARAh), Physica B, 2000, 276-278, 680-681. Program available from: ftp://ftp.ill.fr/pub/dif/sarah

[12] Rodrigues-Carvajal J., BasIreps, Program available from: http://www.ccp14.ac.uk/ccp/web-mirrors/fullprof/php/downloads.html

[13] Sikora W., Pytlik L., Białas F., Malinowski J., Group theory for magnetic structure determination: Recent developments and quadrupolar ordering analysis, J. Alloys Compd., 2007, 442, 61-66

[14] Sikora W., Malinowski J., Figiel H., Symmetry analysis of hydrogen related structural transformations in laves phase intermetallic compounds, J. Alloys Comp., 2007, 446-447, 423-428.

[15] Sikora W., Białas F., Pytlik L., MODY: a program for calculation of symmetry-adapted functions for ordered structures in crystals, 2004, Journal of Applied Crystallography, 37, Part 6, 1015-1019, (Computer programs section)

[16] Jackson D., Chapter 4, In: Classical Electrodynamics, John Wiley & Sons, Inc., 1975.

[17] Matsamura T., Haga Y., Nemoto Y., Nakamura S., Goto T., Suzuki T., Quadrupolar effects in TmTe, Physica B, 1995, 206-207, 380-382

[18] Matsamura T., Nakamura S., Goto T., Shida H., Suzuki T., Quadrupolar Ordering in TmTe, Physica B, 1996, 223-224, 385-388

[19] Matsamura T., Shida H., Suzuki T., Specific heat study of the quadrupolar ordering in TmTe, Physica B, 1997, 230-232, 738-740

[20] Link P., Gukasov A., Mignot J.M., Matsamura T., Suzuki T., Neutron-diffraction study of quadrupole order in TmTe:: observation of a field-induced magnetic superstructure, Physica B, 1999, 259-261, 319

[21] Link P., Matsamura T., Gukasov A., Mignot J.M., Suzuki T., Antiferromagnetism and quadrupolar order in TmTe: a low-temperature neutron-diffraction study, Physica B, 2000, 281-282, 569

[22] Nikolaev A.V., Michel K.H., Microscopic theory of quadrupolar ordering in TmTe, Physical Reviev B, 2001,63, 104-105

[23] Białas F., PhD dissertation, AGH Krakow 2005