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Tilting structures in spinels

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The possible distortions in the spinel structure resulting from rotation of the tetrahedra and octahedra have been investigated by a group-theoretical method. The possibility of the existence of 28 phases of rotation of the tetrahedra and five phases of rotation of the octahedra has been shown. In all these phases the polyhedra are equivalent, but their orientation can be different. Among the phases of the tetrahedra rotation there is one phase of pure rotation, *i.e.* not accompanied by additional (not rotation) distortions of the structure. Of the five phases of the rotation of the octahedra three phases can be obtained only by pure rotation of the octahedra.

1. Introduction

In spinels AB_2X_4 anions X form a dense cubic packing, in the tetrahedral and octahedral voids of which the atoms A and B are distributed. The space group of spinels is $Fd\bar{3}m$ (O_h^7). Tetrahedral cations occupy Wyckoff position 8a with local symmetry $\bar{4}3m$ (T_d), octahedral cations Wyckoff position 16d with local symmetry $\bar{3}m$ (D_{3d}) and anions Wyckoff position 32e with local symmetry $3m$ (C_{3v}). The spinel structure can be represented as a packing of tetrahedra and octahedra (Figs. 1a, 1b). Tetrahedra are placed in the same way as the carbon atoms in diamond; they are not connected with each other (Fig. 1b). Octahedra have common edges with each other and each octahedron is surrounded by six other octahedra (Fig. 1c). Each vertex of the tetrahedron is a vertex of the octahedron.

The rigid framework of the spinel structure from the tetrahedra and octahedra varies weakly with changes in environmental conditions and crystallization. The polyhedral groups of atoms, units (fragments, modules, structural blocks) resistant to external impact, are well known in structural chemistry, crystal chemistry and solid-state physics (Pauling, 1967; Belov, 1947; Urusov, 1987). The modular structure is found in alloys (O'Keeffe & Andersson, 1977), polyphosphides (Jeitschko & Braun, 1978), silicates (Thompson, 1978; Horiuchi *et al.*, 1980), spinelloids (Horioka *et al.*, 1981; Ivanov & Talanov, 2008) and other families of substances (Wells, 1987–1988; Ormont, 1950; Pearson, 1977; Hazen & Finger, 1981; Talanov *et al.*, 2008; Zvyagin, 1993; Blatov *et al.*, 1994; Shevchenko *et al.*, 2009; Zheligovskaya & Bulenkov, 2008*a*,*b*; Ferey, 2000). Today it is clear that the modular structure of matter is a universal feature of matter at all structural levels (Ivanov & Talanov, 2010*a*,*b*,*c*; Ferraris *et al.*, 2005).

By operating the modules, the design of new materials is possible. There have been many approaches to solving this problem (see *e.g.* Zvyagin, 1993; Blatov *et al.*, 1994; Shevchenko *et al.*, 2009; Zheligovskaya & Bulenkov, 2008*a*,*b*; Ferey, 2000; Ivanov & Talanov, 2010*a*,*b*,*c*; Ferraris *et al.*, 2005; Dornberger-Schiff, 1964; Talis & Koptsik, 1990; Burdett, 1980; Glazer, 1972, 1975; Woodward, 1997*a*,*b*; Bock & Müller, 2002). We select group-theoretic methods as the most accurate for the listing of new structures (Gufan, 1982). Dornberger-Schiff (1964) introduced the concept of 'OD structures' (order–disorder structures). Her method is limited and applicable to those cases where the modules are connected by certain operations of partial symmetry (they cannot transform the whole structure into itself). In works (Alexandrov *et al.*, 1981; Aleksandrov, 1976; Aleksandrov *et al.*, 1976; Stokes *et al.*, 2002; Howard & Stokes, 2004, 2005) using group-theoretic methods of the phenomenological theory of phase transitions, different ways of solving the problem of designing low-symmetry distortions of the possible perfect polyhedra packings arising as a result of their rotation are proposed. Examples of such low-symmetry structures are structures of the rotation in perovskites (Shirokov & Torgashev, 2004*a*,*b*).

In terms of possible structures of the rotation, spinels are an extremely interesting object of theoretical study. On the one hand, in the spinel structure, in contrast to the perovskite structure, the octahedra form a more rigid framework, as they are connected not by vertices but by edges. Therefore one can expect a significant reduction in the diversity of structures of rotation in comparison with the perovskite structure. On the other hand, the tetrahedra in the spinel structure can 'freely' rotate, as they are not related structurally to each other. Therefore, we can expect the opposite effect – a large number of possible structures of the rotation. Thus, two opposing tendencies of rotation structures specified by the geometrical singularities of spinel structure require detailed investigation.

There is another circumstance that makes a theoretical study of the possible structures of the rotation in spinels more important and topical. This is due to the fact that a significant

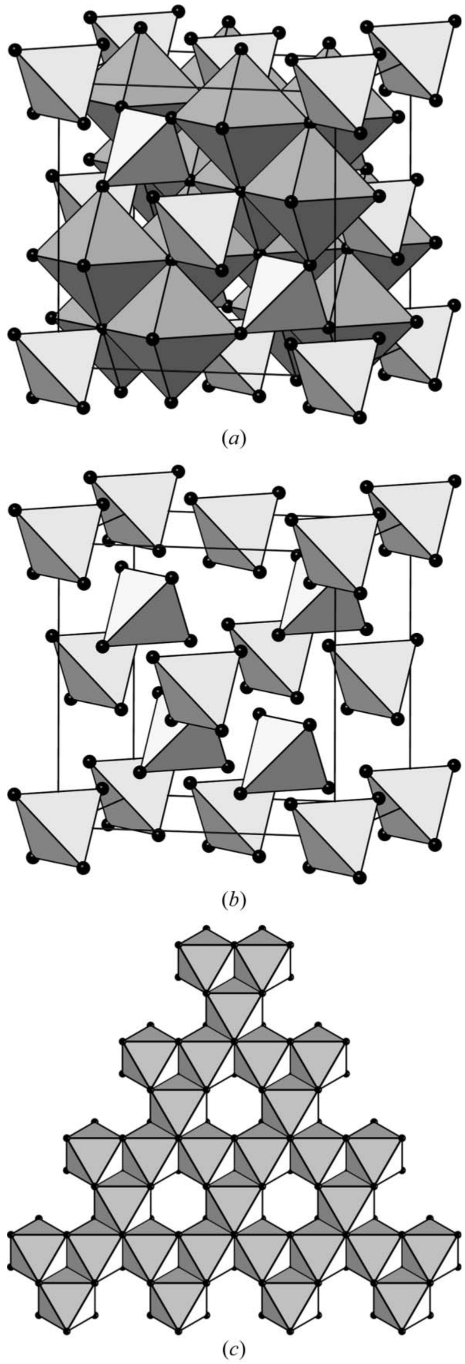

Figure 1
Tetrahedra and octahedra in the spinel structure: (*a*) polyhedral representation, (*b*) packing of the tetrahedra, (*c*) packing of the octahedra (view along the direction [111]).

number of spinels contain atoms *A* and *B* that are transition elements in orbitally degenerate states. According to the Jahn–Teller theorem, any configuration of atoms or ions (except linear) with a degenerate ground electronic state on the orbital angular momentum is unstable with respect to the displacements that lower the symmetry of the configuration. As a result of removing the electron degeneracy, tetrahedra and octahedra, in the centres of which there are the cations *A* and *B*, have to become distorted. If the concentration of the cations of transition elements is sufficient, then at a certain temperature due to the interaction of elementary distortions the cooperative Jahn–Teller effect arises – a structural phase transition accompanied by deformation of the crystal. The microscopic nature of a large number of structural transformations in spinels is precisely due to this effect (Bersuker, 1987; Krupichka, 1976). One of the structural mechanisms of the cooperative Jahn–Teller effect may be a rotation of the tetrahedra and octahedra.

The aim of this work is a group-theoretical study of structures of rotation of tetrahedra and octahedra in spinels.

2. Structures of rotation of the tetrahedra in spinel

Consider rotation of the tetrahedra in the spinel structure, whose centres occupy Wyckoff position 8*a*. We restrict ourselves to the task, including selected points k_9 (L), k_{10} (X), k_{11} (Γ) of the Brillouin zone (designation given by Kovalev, 1965, 1993). Rotations of the tetrahedra in position 8*a* are described by the composition of representations $\boldsymbol{\tau}_9$ (F_{1g}) for the Γ point (proper rotation) and permutational representation of position 8*a* in the extended cell. The translations of the extended cell ($\mathbf{a}_j$) are defined from equations $\exp\,(i\mathbf{k}_L\mathbf{a}_j) = 1$, where $\mathbf{k}_L$ are vectors of all beams L of stars $\{\mathbf{k}\}$, entering the channel of phase transition.

This composition consists of the following irreducible representations:[1]

$$\mathbf{k}_9(\tau_2+\tau_3+\tau_5+\tau_6)+\mathbf{k}_{10}(\tau_1+\tau_2+\tau_4)+\mathbf{k}_{11}(\tau_8+\tau_9). \quad (1)$$

Rotation of the tetrahedra in the spinel structure can be realized only as a displacement of the anions *X*, surrounding the site 8*a*, which occupy a site 32*e* in the spinel structure. Therefore, in the composition of the reducible representations for such rotations only those irreducible representations (IRs) may be included, listed in equation (1), that will be kept in the mechanical representation, built on the displacements of the anions *X*. The composition of the mechanical representation for Wyckoff positions 32*e* of the space group $Fd\bar{3}m$ is as follows:

$$\begin{aligned}&\mathbf{k}_9(3\tau_1+\tau_2+\tau_3+3\tau_4+4\tau_5+4\tau_6)+\mathbf{k}_{10}(4\tau_3+2\tau_4+3\tau_1+3\tau_2)\\&\quad+\mathbf{k}_{11}(\tau_1(A_{1g})+\tau_4(A_{2u})+\tau_5(E_g)+\tau_6(E_u)\\&\quad+2\tau_7(F_{2g})+\tau_8(F_{2u})+\tau_9(F_{1g})+2\tau_{10}(F_{1u})). \quad (2)\end{aligned}$$

From comparison of equations (1) and (2) it follows that the order parameters (OPs) for the structures of the rotation can be OPs that are transformed according to all representations given in equation (1).

IRs $\mathbf{k}_9$: τ_2, τ_3 are four dimensional; $\mathbf{k}_9$: τ_5, τ_6 eight dimensional; all IR $\mathbf{k}_{10}$ six dimensional; $\mathbf{k}_{11}$ one, two and three dimensional. Consider an abstract 48-dimensional parameter

[1] The correspondence of designations by Kovalev and Miller & Love [which is used in the program *ISOTROPY* (Stokes & Hatch, 2007)] is as follows: for k_9 (L): $\tau_1 - L1+$, $\tau_2 - L1-$, $\tau_3 - L2+$, $\tau_4 - L2-$, $\tau_5 - L3+$, $\tau_6 - L3-$; for k_{10} (X): $\tau_1 - X3$, $\tau_2 - X4$, $\tau_3 - X1$, $\tau_4 - X2$; for k_{11} (Γ): $k_{11}t_1$ (A_{1g}) − GM1+, $k_{11}t_2$ (A_{1u}) − GM1−, $k_{11}t_3$ (A_{2g}) − GM2+, $k_{11}t_4$ (A_{2u}) − GM2−, $k_{11}t_5$ (E_g) − GM3+, $k_{11}t_6$ (E_u) − GM3−, $k_{11}t_7$ (F_{2g}) − GM5+, $k_{11}t_8$ (F_{2u}) − GM5−, $k_{11}t_9$ (F_{1g}) − GM4+, $k_{11}t_{10}$ (F_{1u}) − GM4−.

Table 1
Low-symmetry phases formed by tetrahedra tilting in the spinel structure.

Designations for order parameters: $\mathbf{k}_9 - \eta$; $\mathbf{k}_{10} - \varphi$, $\mathbf{k}_{11} - \xi$. The superscript index after the closing parenthesis is the representation number according to Kovalev (1965, 1993), $\varepsilon = [2 + (3^{1/2})]$. V'/V is the change of primitive cell volume as result of structural phase transition. The phase of pure tilting is given in bold.

Phase	OP	Improper OP	Symbol of space group	V'/V	Translations of primitive cell of the $Fd\bar{3}m$ structure
1	$(\xi, -\xi, \xi)^9$	$(\xi, -\xi, \xi)^7$	$R\bar{3}$ (No. 148)	1	$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$
2	$(\xi, -\xi, \xi)^8$	$(\xi, -\xi, \xi)^7$	$R32$ (No. 155)	1	$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$
3	$(0, \xi, 0)^8$	$(\xi, \varepsilon\xi)^5$	$I\bar{4}2d$ (No. 122)	1	$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$
4	$(0, \xi, 0)^9$	$(\xi, \varepsilon\xi)^5$	$I4_1/a$ (No. 88)	1	$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$
5	$(\xi, \xi, 0)^8$	$(\xi, -\xi)^5\ (0, 0, \xi)^7\ (\xi, -\xi, 0)^{10}$	$Ima2$ (No. 46)	1	$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$
6	$(\xi, 0, \xi)^9$	$(\xi, \varepsilon\xi)^5\ (\xi_1, \xi_2, -\xi_1)^7$	$C2/m$ (No. 12)	1	$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$
7	$(\xi_1, \xi_2, \xi_3)^9$	$(\xi_1, \xi_2)^5\ (\xi_1, \xi_2, \xi_3)^7$	$P\bar{1}$ (No. 2)	1	$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$
8	$(0, \xi_1, \xi_2)^8$	$(\xi_1, \xi_2)^5\ (\xi, 0, 0)^7\ (\xi, 0, 0)^9\ (0, \xi_1, \xi_2)^{10}$	Cc (No. 9)	1	$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$
9	$(\xi_1, -\xi_1, \xi_2)^8$	$(\xi, -\xi)^5\ (\xi, -\xi)^6\ (\xi_1, -\xi_1, \xi_2)^7\ (\xi, \xi, 0)^9$ $(\xi, \xi, 0)^{10}$	$C2$ (No. 5)	1	$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$
10	$(0, 0, \eta, 0)^2$	$(\xi, -\xi, \xi)^7$	$R\bar{3}c$ (No. 167)	2	$\mathbf{a}_1, 2\mathbf{a}_2, \mathbf{a}_3$
11	$(0, 0, \eta, 0)^3$	$(\xi, -\xi, \xi)^7$	$R\bar{3}c$ (No. 167)	2	$\mathbf{a}_1, 2\mathbf{a}_2, \mathbf{a}_3$
12	$(0, \eta, 0, 0, 0, \eta, 0, 0)^5$	$(0, 0, \eta, 0)^3\ (\xi, -\xi)^5\ (\xi_1, -\xi_1, 0)^7\ (\xi, \xi, 0)^9$	$C2/c$ (No. 15)	2	$\mathbf{a}_1, \mathbf{a}_2, 2\mathbf{a}_3$
13	$(0, \eta, 0, 0, 0, \eta, 0, 0)^6$	$(0, \eta, 0, 0)^2\ (\xi, -\xi)^5\ (\xi_1, \xi_1, \xi_2)^7\ (\xi, \xi, 0)^9$	$C2/c$ (No. 15)	2	$\mathbf{a}_1 + \mathbf{a}_3, \mathbf{a}_2 + \mathbf{a}_3, 2\mathbf{a}_3$
14	$(\varphi, \varphi, 0, 0, 0, 0)^4$	$(\xi, -\xi)^5\ (0, 0, \xi)^7$	$Pbnn$ (No. 52)	2	$\mathbf{a}_1, \mathbf{a}_2 + \mathbf{a}_3, 2\mathbf{a}_3$
15	$(0, \varphi, 0, 0, 0, 0)^1$	$(\xi, -\xi)^5\ (\xi, -\xi)^6$	$P4_122$ (No. 91), $P4_322$ (No. 95)	2	$\mathbf{a}_1, \mathbf{a}_2 + \mathbf{a}_3, 2\mathbf{a}_3$
16	$(\varphi, -\varphi, 0, 0, 0, 0)^1$	$(\xi, -\xi)^5\ (0, 0, \xi)^7$	$Pcnm$ (No. 53)	2	$\mathbf{a}_1, \mathbf{a}_2 + \mathbf{a}_3, 2\mathbf{a}_3$
17	$\boldsymbol{(\varphi, 0, -\varphi, 0, -\varphi, 0)^1}$		$P4_332$ (No. 212), $P4_132$ (No. 213)	4	$\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3, 2\mathbf{a}_2, 2\mathbf{a}_3$
18	$(0, 0, \varphi, 0, 0, 0)^2$	$(\xi, \varepsilon\xi)^5\ (\xi, \varepsilon\xi)^6$	$P4_12_12$ (No. 92), $P4_32_12$ (No. 96)	2	$\mathbf{a}_1 + \mathbf{a}_3, \mathbf{a}_2, 2\mathbf{a}_3$
19	$(\varphi, \varphi, 0, 0, 0, 0)^2$	$(\xi, -\xi)^5\ (0, 0, \xi)^7$	$Pcmn$ (No. 62)	2	$\mathbf{a}_1, \mathbf{a}_2 + \mathbf{a}_3, 2\mathbf{a}_3$
20	$(\varphi_1, \varphi_2, 0, 0, 0, 0)^1$	$(\xi, -\xi)^5\ (\xi, -\xi)^6\ (0, 0, \xi)^7\ (0, 0, \xi)^8$	$P222_1$ (No. 17)	2	$\mathbf{a}_1, \mathbf{a}_2 + \mathbf{a}_3, 2\mathbf{a}_3$
21	$(0, 0, \varphi_1, \varphi_2, 0, 0)^2$	$(\xi, \varepsilon\xi)^5\ (\xi, \varepsilon\xi)^6\ (0, \xi, 0)^7\ (0, \xi, 0)^8$	$P2_12_12_1$ (No. 19)	2	$\mathbf{a}_1 + \mathbf{a}_3, \mathbf{a}_2, 2\mathbf{a}_3$
22	$(0, \varphi_1, 0, \varphi_2, 0, -\varphi_1)^1\ (0, \varphi, 0, 0, 0, -\varphi)^2$	$(\xi, \varepsilon\xi)^5\ (\xi, \varepsilon\xi)^6$	$P4_12_12$ (No. 92) $P4_32_12$ (No. 96)	4	$\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3, 2\mathbf{a}_2, 2\mathbf{a}_3$
23	$(\varphi, \varphi, 0, 0, 0, 0)^4\ (\varphi, \varphi, 0, 0, 0, 0)^1$ $(\varphi, \varphi, 0, 0, 0, 0)^1\ (\xi, \xi, 0)^9$ $(\varphi, \varphi, 0, 0, 0, 0)^4\ (\xi, \xi, 0)^9$	$(\xi, -\xi)^5\ (\xi_1, -\xi_1, \xi_2)^7\ (\xi, \xi, 0)^9$ $(\varphi, \varphi, 0, 0, 0, 0)^4\ (\xi, -\xi)^5\ (\xi_1, -\xi_1, \xi_2)^7$ $(\varphi, \varphi, 0, 0, 0, 0)^1(\xi, -\xi)^5\ (\xi_1, -\xi_1, \xi_2)^7$	$P2/c$ (No. 13)	2	$\mathbf{a}_1, \mathbf{a}_2 + \mathbf{a}_3, 2\mathbf{a}_3$
24	$(0, 0, \varphi, \varphi, 0, 0)^4\ (0, 0, \varphi, -\varphi, 0, 0)^1$ $(0, 0, \varphi, \varphi, 0, 0)^4\ (\xi, 0, -\xi)^8$ $(0, 0, \varphi, -\varphi, 0, 0)^1\ (\xi, 0, -\xi)^8$	$(\xi, \varepsilon\xi)^5\ (0, \xi, 0)^7\ (\xi, 0, -\xi)^8\ (\xi, 0, \xi)^{10}$ $(0, 0, \varphi, -\varphi, 0, 0)^1\ (\xi, \varepsilon\xi)^5\ (0, \xi, 0)^7\ (\xi, 0, \xi)^{10}$ $(0, 0, \varphi, \varphi, 0, 0)^4\ (\xi, \varepsilon\xi)^5\ (0, \xi, 0)^7\ (\xi, 0, \xi)^{10}$	$Pnc2$ (No. 30)	2	$\mathbf{a}_1 + \mathbf{a}_3, \mathbf{a}_2, 2\mathbf{a}_3$
25	$(\varphi, \varphi, 0, 0, 0, 0)^2\ (\varphi, \varphi, 0, 0, 0, 0)^4$ $(\varphi, \varphi, 0, 0, 0, 0)^4\ (\xi, \xi, 0)^9$ $(\varphi, \varphi, 0, 0, 0, 0)^2\ (\xi, \xi, 0)^9$	$(\xi, -\xi)^5\ (\xi_1, -\xi_1, \xi_2)^7\ (\xi, \xi, 0)^9$ $(\varphi, \varphi, 0, 0, 0, 0)^2\ (\xi, -\xi)^5\ (\xi_1, -\xi_1, \xi_2)^7$ $(\varphi, \varphi, 0, 0, 0, 0)^4\ (\xi, -\xi)^5\ (\xi_1, -\xi_1, \xi_2)^7$	$P2_1/c$ (No. 14)	2	$\mathbf{a}_1, \mathbf{a}_2 + \mathbf{a}_3, 2\mathbf{a}_3$
26	$(0, 0, 0, 0, \varphi, \varphi)^1\ (0, 0, 0, 0, \varphi, \varphi)^2$ $(0, 0, 0, 0, \varphi, \varphi)^1\ (\xi, 0, 0)^9$ $(0, 0, 0, 0, \varphi, \varphi)^2\ (\xi, 0, 0)^9$	$(\xi_1, \xi_2)^5\ (\xi, 0, 0)^7\ (\xi, 0, 0)^9$ $(0, 0, 0, 0, \varphi, \varphi)^2\ (\xi_1, \xi_2)^5\ (\xi, 0, 0)^7$ $(0, 0, 0, 0, \varphi, \varphi)^1\ (\xi_1, \xi_2)^5\ (\xi, 0, 0)^7$	$P2_1/c$ (No. 14)	2	$\mathbf{a}_1 + \mathbf{a}_2, 2\mathbf{a}_2, \mathbf{a}_3$
27	$(0, 0, 0, 0, 0, \varphi)^1\ (0, 0, 0, 0, \varphi, 0)^2$ $(0, 0, 0, 0, 0, \varphi)^1\ (\xi, 0, 0)^9$ $(0, 0, 0, 0, \varphi, 0)^2\ (\xi, 0, 0)^9$	$(\varepsilon\xi, \xi)^5\ (\varepsilon\xi, \xi)^6\ (\xi, 0, 0)^9\ (\xi, 0, 0)^{10}$ $(0, 0, 0, 0, \varphi, 0)^2\ (\varepsilon\xi, \xi)^5\ (\varepsilon\xi, \xi)^6\ (\xi, 0, 0)^{10}$ $(0, 0, 0, 0, 0, \varphi)^1\ (\varepsilon\xi, \xi)^5\ (\varepsilon\xi, \xi)^6\ (\xi, 0, 0)^{10}$	$P4_1$ (No. 76), $P4_3$ (No. 78)	2	$\mathbf{a}_1 + \mathbf{a}_2, 2\mathbf{a}_2, \mathbf{a}_3$
28	$(\varphi, \varphi, 0, 0, 0, 0)^2\ (\varphi, \varphi, 0, 0, 0, 0)^4$ $(\xi, 0, -\xi)^8$	$(\xi, \varepsilon\xi)^5\ (0, \xi, 0)^7\ (\xi, 0, \xi)^{10}$	$Pna2_1$ (No. 33)	2	$\mathbf{a}_1 + \mathbf{a}_3, \mathbf{a}_2, 2\mathbf{a}_3$

of the order with composition as given in equation (1). From the calculations it follows that, with such an OP, 164 types of low-symmetry phases can exist. Among them there is always the lowest-symmetry phase in which all 48 components of the OP are nonzero and between them there are no relations. These phases can be realized not only by a set [equation (1)], but also by a large number of variants of representations from the set [equation (2)]. Therefore there is no reason to consider that this phase can be obtained by the mechanism of rotation of the tetrahedra, although it is in the list of low-symmetry phases.

Consider, as in Shirokov & Torgashev (2004*a*,*b*), only the structure of the rotation, *i.e.* such distortions of the tetrahedra that will make them equivalent. This condition means that, in the model considered, rotation of the tetrahedra should not lead to their ordering. For this purpose, from a complete list of 164 low-symmetry phases, we choose only those that satisfy this requirement. These phases will number 28. The parameters for them are given in Table 1. The second column of Table 1 shows the OPs which determine the symmetry of the low-symmetry phase. In the third column the improper OPs are given, *i.e.* the parameters of the order which appear due to nonlinear interaction with the main (critical) OP. Phase numbers 1–21 are characterized by a single OP transformed according to one irreducible representation. Phase numbers 22–27 are characterized by two OPs and phase number 28 by three OPs. Phase numbers 22–27 with two OPs can be realized in different ways in which the main parameters of the order are two of the OPs given in the third column. Each of these phases can be realized by any pair of three OPs, taking into account the improper OP (see Table 1). A question of choosing the OP in this case will be the quantitative question, *i.e.* any two of OPs with the highest meaning in absolute value are chosen. But for phase number 28 the situation is different. Any pair of three OPs shown in this table (G_D No. 28) changes the symmetry. Therefore, this phase is a phase with three OPs.

The connection of the OP for the obtained low-symmetry phase caused by tetrahedra rotation with the displacements of spinel atoms is given in Table 2. If an IR is included several times in the mechanical representation then different kinds of connections for one OP are written in square brackets.

3. Structures of rotation of the octahedra in spinel

Consider rotation of the octahedra in spinels. In the spinel structure the centres of the octahedra are located in Wyckoff position 16d. For the composition of representations – $\boldsymbol{\tau}_9$ (F_{1g}) for point k_{11} (Γ) of the Brillouin zone and permutation

Table 2
Connection of order parameters with atom displacements in tetrahedra rotation structures.

Designations for order parameters: $\mathbf{k}_9 - \eta$; $\mathbf{k}_{10} - \varphi$; $\mathbf{k}_{11} - \xi$. The superscript index is the representation number according to Kovalev (1965, 1993). If this irreducible representation is included several times in the mechanical representation then in this case different expressions for OPs with the same symmetry are given in square brackets. Designations of Wyckoff positions of coordinates: a_1 = [0, 0, 0], d_1 = [7/8, 11/8, 1/8], d_2 = [13/8, 3/8, 3/8], d_3 = [3/8, 13/8, 3/8], d_5 = [11/8, 11/8, 5/8], $e_1 = [q, q, q]$, $e_2 = [1/2 - q, 1/2 - q, q]$, $e_3 = [-q, -q, q]$, $e_4 = [-q - 1/2, -q - 1/2, q]$, $e_7 = [-q + 3/4, -q + 3/4, -q + 1/4]$, $e_8 = [q + 1/4, q + 1/4, -q + 1/4]$, where q is the free parameter of Wyckoff position 32e. Additional indices x, y, z correspond to coordinates of atom displacements in the low-symmetry phase relative to their positions in the high-symmetry phase. Wyckoff positions in low-symmetry phases have been emphasized in bold italics.

	Wyckoff position		
Phase	8a	16d	32e
1	***2(c):*** $\xi^7 = 4a_{1x}$	***1(b), 3(e)***	***2(c), 6(f):*** $\xi^1 = -2(3^{1/2})(-e_{1x} + e_{1y} + e_{1z} + e_{2x})$, $\xi^7 = [2(e_{1x} + e_{2x} - e_{1y} + e_{1z}), 2(2^{1/2})(e_{1z} - e_{2x})]$, $\xi^9 = 2(2^{1/2})(e_{1x} + e_{1y})$
2	***2(c):*** $\xi^7 = 4a_{1x}$	***1(b), 3(e):*** $\xi^8 = 4d_{1y}$	***2(c), 6(f):*** $\xi^8 = 2(2^{1/2})(e_{1x} + e_{1y})$, $\xi^1 = -2(3^{1/2})(-e_{1x} + e_{1y} + e_{1z} + e_{2x})$, $\xi^7 = [2(e_{1x} + e_{2x} - e_{1y} + e_{1z}), 2(2^{1/2})(e_{1z} - e_{2x})]$
3	***4(b)***	***8(d):*** $\xi^8 = -8d_{1x}$	***16(e):*** $\xi^8 = -4(2^{1/2})(e_{1z} + e_{1x})$, $\xi^1 = 8/(3^{1/2})(e_{1x} - e_{1y} - e_{1z})$, $\xi^5 = 2[1 - 1/(3^{1/2})](2e_{1y} + e_{1x} - e_{1z})$
4	***4(a)***	***8(d)***	***16(f):*** $\xi^9 = -4(2^{1/2})(e_{1z} + e_{1x})$, $\xi^1 = 8/(3^{1/2})(e_{1x} - e_{1y} - e_{1z})$, $\xi^5 = 2[1 - 1/(3^{1/2})](2e_{1y} + e_{1x} - e_{1z})$
5	***4(b):*** $\xi^7 = 4a_{1z}$, $\xi^{10} = 4a_{1x}$	***4(a), 4(b):*** $\xi^8 = 2(-d_{1x} + d_{2x} + d_{2z})$, $\xi^{10} = [2(2^{1/2})(d_{1x} + d_{2x})$, $2(-d_{1x} + d_{2x} - d_{2z})]$	***4(b), 4(b), 8(c):*** $\xi^8 = -(2^{1/2})(e_{1z} + e_{1x} - e_{2z} - e_{7x} + e_{2x} + e_{7y})$, $\xi^1 = 2/[(3^{1/2})2](2e_{1x} - e_{1z} - 2e_{2x} + 2e_{7x} + 2e_{7y} + 2e_{7z} - e_{2z})$, $\xi^5 = 2/(3^{1/2})(e_{7x} + e_{7y} + e_{1x} - 2e_{7z} + e_{1z} - e_{2x} + e_{2z})$, $\xi^7 = [2(e_{1z} + e_{2z} + 2e_{7z}), 2(2^{1/2})(e_{1x} - e_{7x} - e_{2x} - e_{7y})]$, $\xi^{10} = [2(e_{1x} + e_{2x} + e_{7x} - e_{7y}), (2^{1/2})(e_{1z} - e_{1x} - e_{2z} + e_{7x} - e_{2x} - e_{7y})]$
6	***4(i):*** $\xi_1{}^7 = 4a_{1x}$, $\xi_2{}^7 = 4a_{1y}$	***2(b), 2(d), 4(f)***	***4(i), 4(i), 8(j):*** $\xi^9 = (2^{1/2})(e_{8x} - e_{8y} - e_{2x} + e_{2z} + e_{1x} + e_{1y})$, $\xi^1 = -2/(3^{1/2})(2e_{2x} - 2e_{2y} + 2e_{2z} + 2e_{8x} + e_{8y} + e_{1y} - 2e_{1x})$, $\xi^5 = -[1 - 1/(3^{1/2})](e_{2x} + e_{8x} + e_{2z} - e_{1x} - e_{1y} - e_{8y} + 2e_{2y})$, $\xi_1{}^7 = [2(e_{1x} + e_{2x} - e_{2z} + e_{8x}), (2^{1/2})(-e_{8x} - e_{8y} + e_{2x} - e_{2z} - e_{1x} + e_{1y})]$, $\xi_2{}^7 = [2(e_{1y} + 2e_{2y} + e_{8y}), -2(2^{1/2})(e_{8x} - e_{2x} - e_{2z} - e_{1x})]$
7	***2(i):*** $\xi_1{}^7 = 4a_{1x}$, $\xi_2{}^7 = 4a_{1y}$, $\xi_3{}^7 = 4a_{1z}$	***1(e), 1(f), 1(g), 1(h)***	***2(i), 2(i), 2(i), 2(i):*** $\xi_1{}^9 = -(2^{1/2})(e_{7y} + e_{8y} - e_{2y} - e_{1y} + e_{1z} - e_{2z} - e_{7z} + e_{8z})$, $\xi_2{}^9 = (2^{1/2})(-e_{1z} + e_{2z} - e_{1x} - e_{2x} - e_{7z} + e_{7x} + e_{8x} + e_{8z})$, $\xi_3{}^9 = (2^{1/2})(e_{7y} - e_{8y} - e_{2y} + e_{1y} + e_{1x} - e_{2x} - e_{7x} + e_{8x})$, $\xi^1 = -2/(3^{1/2})(-e_{1x} + e_{1y} + e_{1z} + e_{2x} - e_{2y} + e_{2z} - e_{7x} - e_{7y} - e_{7z} + e_{8x} + e_{8y} - e_{8z})$, $\xi_1{}^5 = [1 + 1/(3^{1/2})][e_{7x} - 2e_{7y} - e_{8x} + e_{7z} - 2e_{2y} - e_{2z} + e_{1x} + e_{8z} + 2e_{1y} - e_{2x} - e_{1z}$ $+ 2e_{8y} + (3^{1/2})(e_{7y} - e_{7z} + e_{2y} + e_{2z} - e_{8z} - e_{1y} + e_{1z} - e_{8y})]$, $\xi_2{}^5 = [1 + 1/(3^{1/2})][-e_{1y} + 2e_{2x} - e_{1z} - e_{2z} + e_{7y} - 2e_{7x} + 2e_{8x} + e_{7z} + e_{2y} - 2e_{1x} - e_{8y}$ $+ e_{8z} + (3^{1/2})(-e_{2x} + e_{1z} + e_{2z} + e_{7x} - e_{8x} - e_{7z} + e_{1x} - e_{8z})]$, $\xi_1{}^7 = [2(e_{1x} + e_{2x} + e_{7x} + e_{8x}), (2^{1/2})(-e_{7y} - e_{8y} + e_{2y} + e_{1y} + e_{1z} - e_{2z} - e_{7z} + e_{8z})]$, $\xi_2{}^7 = [2(e_{1y} + e_{2y} + e_{7y} + e_{8y}), -(2^{1/2})(e_{1z} - e_{2z} - e_{1x} - e_{2x} + e_{7z} + e_{7x} + e_{8x} - e_{8z})]$, $\xi_3{}^7 = [2(e_{1z} + e_{2z} + e_{7z} + e_{8z}), (2^{1/2})(-e_{7y} + e_{8y} + e_{2y} - e_{1y} + e_{1x} - e_{2x} - e_{7x} + e_{8x})]$
8	***4(a):*** $\xi^7 = 4a_{1x}$, $\xi_1{}^{10} = 4a_{1y}$, $\xi_2{}^{10} = 4a_{1z}$	***4(a), 4(a):*** $\xi_1{}^8 = 2(-d_{1x} - d_{1z} + d_{2x} + d_{2z})$, $\xi_2{}^8 = 2(-d_{1x} + d_{1y} - d_{2x} - d_{2y})$, $\xi_1{}^{10} = [2(2^{1/2})(d_{1y} + d_{2y})$, $2(d_{1x} - d_{1z} - d_{2x} + d_{2z})]$, $\xi_2{}^{10} = [2(2^{1/2})(d_{1z} + d_{2z})$, $2(-d_{1x} - d_{1y} - d_{2x} + d_{2y})]$	***4(a), 4(a), 4(a), 4(a):*** $\xi_1{}^8 = -(2^{1/2})(-e_{4z} + e_{3z} - e_{2z} + e_{1z} + e_{4x} + e_{3x} + e_{2x} + e_{1x})$, $\xi_2{}^8 = -(2^{1/2})(e_{4y} - e_{3y} + e_{2y} - e_{1y} + e_{4x} - e_{3x} + e_{2x} - e_{1x})$, $\xi^1 = 2/(3^{1/2})(e_{1x} - e_{1y} - e_{1z} - e_{2x} + e_{2y} - e_{2z} - e_{3x} + e_{3y} + e_{3z} + e_{4x} - e_{4y} + e_{4z})$, $\xi_1{}^5 = [-1 + 1/(3^{1/2})][-2e_{1x} - e_{1y} - e_{1z} + 2e_{2x} + e_{2y} - e_{2z} + 2e_{3x} + e_{3y} + e_{3z} - 2e_{4x}$ $- e_{4y} + e_{4z} + (3^{1/2})(-e_{1x} - e_{1z} + e_{2x} - e_{2z} + e_{3x} + e_{3z} - e_{4x} + e_{4z})]$, $\xi_2{}^5 = [-1 + 1/(3^{1/2})][-e_{1x} - 2e_{1y} + e_{1z} + e_{2x} + 2e_{2y} + e_{2z} + e_{3x} + 2e_{3y} - e_{3z} - e_{4x} - 2e_{4y}$ $- e_{4z} + (3^{1/2})(-e_{1y} + e_{1z} + e_{2y} + e_{2z} + e_{3y} - e_{3z} - e_{4y} - e_{4z})]$, $\xi^7 = [2(e_{1x} + e_{2x} - e_{3x} - e_{4x}), -(2^{1/2})(-e_{4z} + e_{4y} + e_{3z} + e_{3y} + e_{2z} - e_{2y} - e_{1z} - e_{1y})]$, $\xi^9 = -(2^{1/2})(e_{4z} + e_{4y} - e_{3z} + e_{3y} - e_{2z} - e_{2y} + e_{1z} - e_{1y})$, $\xi_1{}^{10} = [2(e_{1y} + e_{2y} + e_{3y} + e_{4y}), (2^{1/2})(e_{4z} - e_{3z} + e_{2z} - e_{1z} + e_{4x} + e_{3x} + e_{2x} + e_{1x})]$, $\xi_2{}^{10} = [2(e_{1z} + e_{2z} + e_{3z} + e_{4z}), -(2^{1/2})(-e_{4y} + e_{3y} - e_{2y} + e_{1y} + e_{4x} - e_{3x} + e_{2x} - e_{1x})]$

Table 2 (continued)

	Wyckoff position		
Phase	8*a*	16*d*	32*e*
9	***4(c):*** $\xi_1{}^7 = 4(a_{1x} - a_{1y})$, $\xi_2{}^7 = 4a_{1z}$, $\xi^{10} = 2(a_{1x} + a_{1y})$	***2(a), 2(b), 4(c):*** $\xi_1{}^8 = d_{1x} + d_{1y} + 2d_{1z} - d_{2x} - d_{3x}$, $\xi_2{}^8 = 2(-d_{1x} + d_{1y} - d_{2x} + d_{3x})$, $\xi^6 = (3^{1/2})(d_{1x} - d_{1y} - d_{2x} + d_{3x})$, $\xi^{10} = [(2^{1/2})(d_{1x} + d_{1y} + d_{2x} + d_{3x})$, $d_{1x} + d_{1y} - 2d_{1z} - d_{2x} - d_{3x}]$	***4(c), 4(c), 4(c), 4(c):*** $\xi_1{}^8 = -1/(2^{1/2})(2e_{8z} + e_{8y} - 2e_{7z} + e_{7y} - e_{2x} - e_{1x} - e_{2y} - e_{1y} + e_{8x} + e_{7x})$, $\xi_2{}^8 = (2^{1/2})(e_{8x} - e_{8y} + e_{7y} - e_{2x} + e_{1x} - e_{2y} + e_{1y} - e_{7x})$, $\xi^1 = -2/(3^{1/2})(-e_{7x} - e_{7y} - e_{7z} + e_{8x} + e_{8y} - e_{8z} - e_{1x} + e_{1y} + e_{1z} + e_{2x} - e_{2y} + e_{2z})$, $\xi^5 = 1/(3^{1/2})(2e_{2z} - 2e_{8z} + e_{7y} - e_{2x} - e_{8x} + e_{1x} + e_{2y} + 2e_{1z} - 2e_{7z} - e_{1y} + e_{7x} - e_{8y})$, $\xi^6 = -e_{8x} + e_{7x} - e_{7y} - e_{2y} + e_{1x} + e_{8y} + e_{1y} - e_{2x}$, $\xi_1{}^7 = [e_{1x} + e_{2x} - e_{1y} - e_{2y} + e_{7x} + e_{8x} - e_{8y} - e_{7y}, (2^{1/2})/2(-e_{8y} - e_{7y} - e_{2x}$ $- e_{1x} - 2e_{2z} + e_{2y} + 2e_{1z} + e_{1y} + e_{8x} + e_{7x})]$, $\xi_2{}^7 = [2(e_{1z} + e_{2z} + e_{7z} + e_{8z}), (2^{1/2})(e_{8x} + e_{8y} - e_{7y} - e_{2x} + e_{1x} + e_{2y} - e_{1y} - e_{7x})]$, $\xi^9 = (2^{1/2})/2(-e_{8y} - e_{7y} - e_{2x} - e_{1x} + 2e_{2z} + e_{2y} - 2e_{1z} + e_{1y} + e_{8x} + e_{7x})$, $\xi^{10} = [e_{1x} + e_{2x} + e_{1y} + e_{2y} + e_{7x} + e_{8x} + e_{8y} + e_{7y}, -(2^{1/2})/2(-2e_{8z} + e_{8y} + 2e_{7z} + e_{7y}$ $- e_{2x} - e_{1x} - e_{2y} - e_{1y} + e_{8x} + e_{7x})]$
10	***4(c):*** $\xi^7 = 4a_{1x}$	***2(b), 6(e):*** $\eta^2 = 4(3^{1/2})d_{1y}$	***12(f), 4(c):*** $\eta^2 = -2/(6^{1/2})(e_{1x} + e_{1y})$, $\xi^1 = -2(3^{1/2})(-e_{1x} + e_{1y} + e_{1z} + e_{2x})$, $\xi^7 = [2(e_{1x} + e_{2x} - e_{1y} + e_{1z}), -2(2^{1/2})(e_{2x} - e_{1z})]$
11	***4(c):*** $\xi^7 = 4a_{1x}$	***2(a), 6(d)***	***4(c), 12(f):*** $\eta^3 = -2/(6^{1/2})(e_{1x} + e_{1y})$, $\xi^1 = -2(3^{1/2})(-e_{1x} + e_{1y} + e_{1z} + e_{2x})$, $\xi^7 = [2(e_{1x} + e_{2x} - e_{1y} + e_{1z}), -2(2^{1/2})(e_{2x} - e_{1z})]$
12	***8(f):*** $\eta^5 = 2(a_{1x} + a_{1y})$, $\xi_1{}^7 = 2(a_{1x} - a_{1y})$, $\xi_2{}^7 = 4a_{1z}$	***4(b), 4(c), 4(d), 4(e):*** $\eta^5 = 2(2^{1/2})d_{2x}$	***8(f), 8(f), 8(f), 8(f):*** $\eta^5 = \{-(e_{8y} + e_{7x}), 1/(3^{1/2})[2e_{7y} + 2e_{8x} + e_{7z} - e_{2y} - e_{8z} - e_{2x} + (3^{1/2})(e_{7z} + e_{2y} - e_{8z}$ $+ e_{2x})], [-1 + 1/(3^{1/2})][e_{8z} - 2e_{2x} + e_{7y} + e_{8x} - e_{7z} - 2e_{2y} + (3^{1/2})(-e_{2x} + e_{7y} + e_{8x}$ $+ e_{2y})], 2(e_{1x} + e_{1y})\}$, $\eta^3 = 2(2/3)^{1/2}(e_{2x} + e_{2y} + e_{7y} - e_{7z} + e_{8x} + e_{8z})$, $\xi^1 = -2/(3^{1/2})(-e_{7y} - e_{7z} + e_{8x} + e_{8y} - e_{8z} + e_{1y} + e_{1z} + e_{2x} - e_{2y} + e_{2z} - e_{1x} - e_{7x})$, $\xi^5 = 1/(3^{1/2})(2e_{1z} + e_{7y} + 2e_{2z} - e_{2x} + e_{1x} - 2e_{8z} - e_{8x} + e_{2y} - e_{8y} - 2e_{7z} - e_{1y} + e_{7x})$, $\xi_1{}^7 = [e_{1x} + e_{2x} - e_{1y} - e_{2y} + e_{7x} + e_{8x} - e_{7y} - e_{8y}, (2^{1/2})/2(-e_{7y} - e_{8y} + 2e_{1z} + e_{2y}$ $- 2e_{2z} - e_{1x} - e_{2x} + e_{1y} + e_{7x} + e_{8x})]$, $\xi_2{}^7 = [2(e_{1z} + e_{2z} + e_{7z} + e_{8z}), (2^{1/2})(-e_{7y} + e_{8y} + e_{2y} + e_{1x} - e_{2x} - e_{1y} - e_{7x} + e_{8x})]$, $\xi^9 = (2^{1/2})/2(-e_{7y} - e_{8y} - 2e_{1z} + e_{2y} + 2e_{2z} - e_{1x} - e_{2x} + e_{1y} + e_{7x} + e_{8x})$
13	***8(f):*** $\eta^6 = 2(a_{1x} + a_{1y})$, $\xi_1{}^7 = 2(a_{1x} - a_{1y})$, $\xi_2{}^7 = 4a_{1z}$	***4(d), 4(e), 8(f):*** $\eta^2 = 4/(3^{1/2})(d_{1x} + d_{1z} + d_{3x})$, $\eta^6 = \{(2/3)^{1/2}[2d_{3x} - d_{1z} - d_{1x}$ $+ (3^{1/2})(d_{1z} - d_{1x})]$, $- (2/3)^{1/2}[2d_{3x} - d_{1z} - d_{1x}$ $- (3^{1/2})(d_{1z} - d_{1x})], 2(2^{1/2})d_{1y}\}$	***8(f), 8(f), 8(f), 8(f):*** $\eta^6 = \{-2(e_{7x} + e_{8y}), 1/(3^{1/2})[2e_{7y} + 2e_{8x} + e_{7z} - e_{2y} - e_{8z} - e_{2x} + (3^{1/2})(e_{7z} + e_{2y} - e_{8z}$ $+ e_{2x})], -1/(3^{1/2})[2e_{8x} + e_{7z} - e_{2y} - e_{2x} - e_{8z} + 2e_{7y} + (3^{1/2})(-e_{7z} - e_{2y} - e_{2x} + e_{8z})]$, $2(e_{1x} + e_{1y})\}$, $\eta^2 = 2(2/3)^{1/2}(e_{2x} + e_{2y} + e_{7y} - e_{7z} + e_{8x} + e_{8z})$, $\xi^1 = -2/(3^{1/2})(-e_{7y} - e_{7z} + e_{8x} + e_{8y} - e_{8z} + e_{1y} + e_{1z} + e_{2x} - e_{2y} + e_{2z} - e_{1x} - e_{7x})$, $\xi^5 = 1/(3^{1/2})(2e_{1z} + e_{7y} + 2e_{2z} - e_{2x} + e_{1x} - 2e_{8z} - e_{8x} + e_{2y} - e_{8y} - 2e_{7z} - e_{1y} + e_{7x})$, $\xi_1{}^7 = [e_{1x} + e_{2x} - e_{1y} - e_{2y} + e_{7x} + e_{8x} - e_{7y} - e_{8y}, 1/(2^{1/2})(-e_{7y} - e_{8y} + 2e_{1z} + e_{2y}$ $- 2e_{2z} - e_{1x} - e_{2x} + e_{1y} + e_{7x} + e_{8x})]$, $\xi_2{}^7 = [2(e_{1z} + e_{2z} + e_{7z} + e_{8z}), (2^{1/2})(-e_{7y} + e_{8y} + e_{2y} + e_{1x} - e_{2x} - e_{1y} - e_{7x} + e_{8x})]$, $\xi_2{}^9 = 1/(2^{1/2})(-e_{7y} - e_{8y} - 2e_{1z} + e_{2y} + 2e_{2z} - e_{1x} - e_{2x} + e_{1y} + e_{7x} + e_{8x})$
14	***4(c):*** $\xi^7 = 4a_{1z}$	***4(a), 4(d):*** $\varphi^4 = -4d_{2x}$	***8(e), 8(e):*** $\varphi^4 = [2(e_{1x} + e_{1y} + e_{7x} - e_{7y}), 2(-e_{1x} - e_{1y} + e_{7x} - e_{7y})]$, $\xi^1 = 4/(3^{1/2})(-e_{1z} + e_{7x} + e_{7y} + e_{7z} + e_{1x} - e_{1y})$, $\xi^5 = 2/(3^{1/2})(e_{7y} + e_{1x} + e_{7x} - 2e_{7z} - e_{1y} + 2e_{1z})$, $\xi^7 = [4(e_{1z} + e_{7z}), -2(2^{1/2})(-e_{1x} + e_{1y} + e_{7x} + e_{7y})]$
15	***4(c):*** $\varphi^1 = 4a_{1y}$	***4(a), 4(b):*** $\varphi^1 = -4(d_{1x} + d_{2x})$, $\xi^6 = 2(2^{1/2})(d_{1x} - d_{2x})$	***8(d), 8(d):*** $\varphi^1 = [4(e_{1y} + e_{2y}), 4(e_{1x} + e_{2x}), 4(-e_{1z} + e_{2z})]$, $\xi^1 = -4/(3^{1/2})(-e_{1x} + e_{1y} + e_{1z} + e_{2x} - e_{2y} + e_{2z})$, $\xi^5 = 2/(3^{1/2})(2e_{2z} + e_{1x} - e_{2x} + e_{2y} + 2e_{1z} - e_{1y})$, $\xi^6 = 2(e_{1x} - e_{2x} - e_{2y} + e_{1y})$
16	***4(h):*** $\varphi^1 = 4a_{1x}$, $\xi^7 = 4a_{1z}$	***2(a), 2(d), 4(g):*** $\varphi^1 = 4d_{1x}$	***4(h), 4(h), 8(i):*** $\varphi^1 = [2(e_{1x} + e_{2x} - e_{7x} + e_{7y}), 2(-e_{1x} - e_{2x} + e_{7y} - e_{7x}), 2(e_{1z} - e_{2z})]$, $\xi^1 = 2/(3^{1/2})(2e_{7y} + 2e_{7x} + 2e_{7z} + 2e_{1x} - e_{1z} - 2e_{2x} - e_{2z})$, $\xi^5 = 2/(3^{1/2})(e_{2z} - 2e_{7z} - e_{2x} + e_{1z} + e_{7y} + e_{1x} + e_{7x})$, $\xi^7 = [2(e_{1z} + e_{2z} + 2e_{7z}), -2(2^{1/2})(e_{7x} + e_{7y} + e_{2x} - e_{1x})]$
17	***8(c):*** $\varphi^1 = 4a_{1x}$	***4(a), 12(d):*** $\varphi^1 = 4d_{1x}$	***8(c), 24(e):*** $\varphi^1 = [2(e_{1x} + e_{1z} + e_{3x} - e_{1y}), 2(e_{1y} + e_{1x} - e_{3x} + e_{1z}), 2(e_{1z} - e_{1y} - e_{3x} - e_{1x})]$, $\xi^1 = -2(3^{1/2})(e_{1z} + e_{1y} + e_{3x} - e_{1x})$
18	***4(a):*** $\varphi^2 = 4a_{1z}$	***8(b):*** $\varphi^2 = [4(d_{1x} - d_{1z}), -4(2^{1/2})d_{1y}]$, $\xi^6 = (2^{1/2})[1 - (3^{1/2})](d_{1x} + d_{1z})$	***8(b), 8(b):*** $\varphi^2 = [4(-e_{1z} + e_{2z}), -4(e_{1x} + e_{2x}), 4(e_{1y} + e_{2y})]$, $\xi^1 = -4/(3^{1/2})(-e_{1x} + e_{1y} + e_{1z} + e_{2x} - e_{2y} + e_{2z})$, $\xi^5 = [-1 + 1/(3^{1/2})](e_{1z} + e_{1x} + e_{2x} - 2e_{1y} + e_{2z} + 2e_{2y})$, $\xi^6 = [1 - (3^{1/2})](e_{1x} + e_{1z} - e_{2x} + e_{2z})$
19	***4(c):*** $\varphi^2 = 4a_{1x}$, $\xi^7 = 4a_{1z}$	***4(a), 4(c):*** $\varphi^2 = [-4d_{2x}, -2(2^{1/2})d_{2z}]$	***4(c), 4(c), 8(d):*** $\varphi^2 = [2(e_{1x} + e_{2x} - e_{7x} + e_{7y}), 2(-e_{1x} - e_{2x} + e_{7y} - e_{7x}), 2(e_{1z} - e_{2z})]$, $\xi^1 = 2/(3^{1/2})(2e_{7y} + 2e_{7x} + 2e_{7z} + 2e_{1x} - e_{1z} - 2e_{2x} - e_{2z})$, $\xi^5 = 2/(3^{1/2})(e_{2z} - 2e_{7z} - e_{2x} + e_{1z} + e_{7y} + e_{1x} + e_{7x})$, $\xi^7 = [2(e_{1z} + e_{2z} + 2e_{7z}), -2(2^{1/2})(e_{7x} + e_{7y} + e_{2x} - e_{1x})]$

representation constructed at Wyckoff position 16d in the extended cell on vectors $\mathbf{k}_9$ (L), $\mathbf{k}_{10}$ (X) – we have a set of the following IRs:

$$\mathbf{k}_9(\tau_1+\tau_2+\tau_3+\tau_5+\tau_6)+\mathbf{k}_{10}(\tau_1+\tau_2+\tau_3+\tau_4) + \mathbf{k}_{11}(\tau_3+\tau_5+\tau_7+\tau_9). \quad (3)$$

From the representations of equation (3) it is necessary to remove only $\mathbf{k}_{11}$: τ_3, which is not included in the composition of equation (2). In the permutation representation at Wyckoff position 16d the following IRs are included:

$$\mathbf{k}_9(\tau_1+\tau_4+\tau_5)+\mathbf{k}_{10}(\tau_1+\tau_3)+\mathbf{k}_{11}(\tau_1+\tau_7). \quad (4)$$

Table 2 (continued)

	Wyckoff position		
Phase	8a	16d	32e
20	***4(e):*** $\varphi_1{}^1 = 4a_{1x}$, $\varphi_2{}^1 = 4a_{1y}$, $\xi^7 = 4a_{1z}$	***2(a), 2(b), 2(c), 2(d):*** $\varphi_1{}^1 = 2(d_{1x} - d_{2x} - d_{3x} - d_{5x})$, $\varphi_2{}^1 = 2(-d_{1x} - d_{2x} - d_{3x} + d_{5x})$, $\eta^6 = (2^{1/2})(d_{1x} - d_{2x} + d_{3x} + d_{5x})$, $\xi^8 = 2(-d_{1x} - d_{2x} + d_{3x} - d_{5x})$	***4(e), 4(e), 4(e), 4(e):*** $\varphi_1{}^1 = [2(e_{1x} + e_{2x} - e_{7x} - e_{8x}), 2(e_{1y} + e_{2y} + e_{7y} + e_{8y}), 2(e_{1z} - e_{2z} + e_{7z} - e_{8z})]$, $\varphi_2{}^1 = [2(e_{1y} + e_{2y} - e_{7y} - e_{8y}), 2(e_{1x} + e_{2x} + e_{7x} + e_{8x}), 2(-e_{1z} + e_{2z} + e_{7z} - e_{8z})]$, $\xi^1 = -2/(3^{1/2})(e_{1y} - e_{7x} - e_{7y} - e_{7z} + e_{8x} + e_{8y} + e_{1z} + e_{2x} - e_{2y} + e_{2z} - e_{8z} - e_{1x})$, $\xi^5 = 1/(3^{1/2})(-e_{2x} - e_{8x} + 2e_{1z} - 2e_{8z} + e_{7x} - e_{1y} + e_{2y} + e_{1x} - 2e_{7z} + 2e_{2z} + e_{7y} - e_{8y})$, $\xi^6 = e_{7x} - e_{8x} - e_{2y} + e_{1x} + e_{8y} + e_{1y} - e_{2x} - e_{7y}$, $\xi^7 = [2(e_{1z} + e_{2z} + e_{7z} + e_{8z}), (2^{1/2})(e_{1x} - e_{2x} + e_{8y} - e_{7y} + e_{2y} - e_{1y} + e_{8x} - e_{7x})]$, $\xi^8 = (2^{1/2})(e_{1x} - e_{2x} - e_{8y} + e_{7y} - e_{2y} + e_{1y} + e_{8x} - e_{7x})$
21	***4(a):*** $\varphi^2 = 4a_{1z}$, $\xi^7 = 4a_{1y}$	***4(a), 4(a):*** $\varphi_1{}^2 = [2(d_{1x} - d_{1z} - d_{3x} - d_{3z}),$ $- 2(2^{1/2})(d_{1y} + d_{3y})]$, $\varphi_2{}^2 = [2(d_{1x} - d_{1z} + d_{3x} + d_{3z},$ $- (2^{1/2})(d_{1y} - d_{3y})]$, $\eta^6 = [1 - (3^{1/2})]/(2^{1/2})(d_{1x} + d_{1z}$ $+ d_{3x} - d_{3z})$, $\xi^8 = 2(-d_{1x} - d_{1z} + d_{3x} - d_{3z})$	***4(a), 4(a), 4(a), 4(a):*** $\varphi_1{}^2 = [2(-e_{1z} + e_{2z} + e_{3x} + e_{6x}), 2(-e_{1x} - e_{2x} + e_{3z} - e_{6z}), 2(e_{1y} + e_{2y} + e_{3y} + e_{6y})]$, $\varphi_2{}^2 = [2(e_{1x} - e_{2x} - e_{3z} - e_{6z}), 2(e_{1z} + e_{2z} - e_{3x} + e_{6x}), 2(e_{1y} - e_{2y} + e_{3y} - e_{6y})]$, $\xi^1 = 2/(3^{1/2})(e_{6z} - e_{6y} + e_{6x} + e_{3z} + e_{3y} - e_{3x} - e_{2z} + e_{2y} - e_{2x} - e_{1z} - e_{1y} + e_{1x})$, $\xi^5 = [1 - 1/(3^{1/2})]/2(e_{6x} - e_{2z} - e_{2x} + e_{6z} + e_{3z} - e_{1z} - e_{3x} + e_{1x} - 2e_{3y} + 2e_{1y}$ $- 2e_{2y} + 2e_{6y})$, $\xi^6 = [1 - 1/(3^{1/2})]/2(e_{3x} + e_{2z} - e_{6x} + e_{1x} + e_{3z} - e_{2x} + e_{1z} + e_{6z})$, $\xi^7 = [2(e_{1y} + e_{2y} - e_{3y} - e_{6y}), (2^{1/2})(-e_{1z} + e_{2z} + e_{3z} + e_{2x} + e_{1x} - e_{6z} - e_{3x} - e_{6x})]$, $\xi^8 = (2^{1/2})(-e_{1z} + e_{2z} - e_{3z} - e_{2x} - e_{1x} + e_{6z} - e_{3x} - e_{6x})$
22	***8(b):*** $\varphi^1 = 2(a_{1y} - a_{1z})$, $\varphi^2 = -2(a_{1y} + a_{1z})$	***4(a), 4(a), 8(b):*** $\varphi_1{}^1 = -d_{1x} - d_{2x} - 2d_{2y} + d_{2z}$ $+ d_{5x}$, $\varphi_2{}^1 = 2(-d_{1x} - d_{2x} - d_{2z} - d_{5x})$, $\varphi^2 = [-d_{1x} - d_{2x} + 2d_{2y} + d_{2z}$ $+ d_{5x}, (2^{1/2})(-d_{1x} + d_{2x} - d_{2z} +$ $d_{5x})]$, $\eta^6 = [1 - (3^{1/2})]/(2^{1/2})(d_{1x} - d_{2x}$ $- d_{2z} + d_{5x})$	***8(b), 8(b), 8(b), 8(b):*** $\varphi_1{}^1 = (e_{1y} + e_{2y} - e_{1z} - e_{4x} - e_{5x} + e_{2z} + e_{5y} + e_{4y}, e_{1x} + e_{2x} + e_{1y} - e_{4y} - e_{5y} + e_{2y}$ $- e_{5z} + e_{4z}, - e_{1z} + e_{2z} - e_{1x} + e_{4z} - e_{5z} - e_{2x} + e_{5x} + e_{4x})$, $\varphi_2{}^1 = [2(-e_{1x} + e_{2x} + e_{4z} + e_{5z}), 2(e_{1z} - e_{2z} - e_{4x} + e_{5x}), 2(e_{1y} + e_{2y} + e_{4y} - e_{5y})]$, $\varphi^2 = (-e_{1y} - e_{2y} - e_{1z} - e_{4x} - e_{5x} + e_{2z} - e_{5y} - e_{4y}, - e_{1x} - e_{2x} + e_{1y} - e_{4y} - e_{5y}$ $+ e_{2y} + e_{5z} - e_{4z}, e_{1z} - e_{2z} - e_{1x} + e_{4z} - e_{5z} - e_{2x} - e_{5x} - e_{4x})$, $\xi^1 = 2/(3^{1/2})(e_{1x} - e_{1y} - e_{2x} + e_{2y} - e_{2z} + e_{4x} - e_{4y} + e_{4z} - e_{5x} + e_{5y} + e_{5z} - e_{1z})$, $\xi^5 = [-1 + 1/(3^{1/2})]/2(e_{2z} + e_{2x} - e_{4z} + e_{1z} + e_{5x} - e_{5z} - 2e_{1y} + 2e_{2y} - e_{4x} - e_{1x}$ $- 2e_{4y} + 2e_{5y})$, $\xi^6 = [1 - 1/(3^{1/2})]/2(e_{2z} - e_{2x} + e_{5x} + e_{1x} + e_{5z} + e_{4z} - e_{4x} + e_{1z})$
23	***4(g):*** $\varphi^1 = 2(a_{1x} + a_{1y})$, $\xi_1{}^7 = 2(a_{1x} - a_{1y})$, $\xi_2{}^7 = 4a_{1z}$	***2(b), 2(d) 2(e), 2(f):*** $\varphi^4 = 2(-d_{2x} + d_{3x})$, $\varphi^1 = 2(-d_{2x} - d_{3x})$	***4(g), 4(g), 4(g), 4(g):*** $\varphi^4 = (e_{1x} + e_{1y} - e_{2x} - e_{2y} + e_{7x} - e_{7y} - e_{8x} + e_{8y}, - e_{1x} - e_{1y} + e_{2x} + e_{2y} + e_{7x} - e_{7y}$ $- e_{8x} + e_{8y}, e_{1x} + e_{2x} + e_{1y} + e_{2y} - e_{7x} - e_{8x} - e_{8y} - e_{7y})$, $\varphi^1 = [e_{1y} + e_{2y} + e_{1x} + e_{2x} + e_{7y} + e_{8y} + e_{8x} + e_{7x}, 2(e_{7z} - e_{8z})]$ $\xi^1 = -2/(3^{1/2})(e_{1z} + e_{2x} - e_{2y} + e_{2z} - e_{7x} - e_{7y} - e_{7z} + e_{1y} - e_{1x} + e_{8y} - e_{8z} + e_{8x})$, $\xi^5 = 1/(3^{1/2})(e_{2y} - e_{8x} - e_{1y} + e_{1x} + 2e_{2z} - 2e_{7z} + 2e_{1z} - e_{2x} - 2e_{8z} - e_{8y} + e_{7x} + e_{7y})$, $\xi_1{}^7 = [e_{1x} + e_{2x} + e_{7x} + e_{8x} - e_{2y} - e_{1y} - e_{8y} - e_{7y}, 1/(2^{1/2})(-2e_{2z} + 2e_{1z} - e_{2x} - e_{8y}$ $- e_{7y} + e_{2y} + e_{1y} - e_{1x} + e_{7x} + e_{8x})]$, $\xi_2{}^7 = [2e_{1z} + 2e_{2z} + 2e_{7z} + 2e_{8z}, (2^{1/2})(-e_{2x} - e_{7x} + e_{8x} + e_{8y} - e_{7y} + e_{2y} - e_{1y} + e_{1x})]$, $\xi^9 = 1/(2^{1/2})(2e_{2z} - 2e_{1z} - e_{2x} - e_{8y} - e_{7y} + e_{2y} + e_{1y} - e_{1x} + e_{7x} + e_{8x})$
24	***4(c):*** $\varphi^1 = 2(-a_{1x} + a_{1z})$, $\xi^7 = a_{1y}$, $\xi^{10} = 2(a_{1x} + a_{1z})$	***2(a), 2(b), 4(c):*** $\varphi^4 = 2(-d_{1x} + d_{2x})$, $\varphi^1 = 2(d_{3x} - d_{3z})$, $\xi^8 = (d_{1x} + d_{2x} - d_{3x}$ $- 2d_{3y} - d_{3z})$, $\xi^{10} = [(2^{1/2})(d_{1x} + d_{2x} + d_{3x} + d_{3z})$, $- d_{1x} - d_{2x} + d_{3x} - 2d_{3y} + d_{3z}]$	***4(c), 4(c), 4(c), 4(c):*** $\varphi^4 = (e_{1x} + e_{1z} - e_{2x} + e_{2z} - e_{4x} + e_{4z} - e_{5x} - e_{5z}, - e_{1z} - e_{1x} - e_{4x} + e_{4z} + e_{5x}$ $+ e_{5z} - e_{2x} + e_{2z})$, $\varphi^1 = (-e_{1z} + e_{2z} + e_{4x} + e_{5x} - e_{4z} - e_{5z} + e_{1x} - e_{2x}, -e_{1x} - e_{2x} - e_{4z} + e_{5z} + e_{4x}$ $- e_{5x} + e_{1z} + e_{2z}, 2e_{1y} + 2e_{5y})$, $\xi^1 = 2/(3^{1/2})(e_{1x} - e_{1y} - e_{1z} - e_{2x} + e_{2y} - e_{2z} + e_{4x} - e_{4y} + e_{4z} - e_{5x} + e_{5y} + e_{5z})$, $\xi^5 = [-1 + 1/(3^{1/2})]/2(-e_{4x} + 2e_{5y} - e_{5z} + e_{2x} + e_{1z} - 2e_{1y} + e_{2z} - e_{4z} + e_{5x} + 2e_{2y}$ $- 2e_{4y} - e_{1x})$, $\xi^7 = [2(e_{1y} + e_{2y} - e_{4y} - e_{5y}), -(2^{1/2})(e_{1z} - e_{2z} + e_{4z} - e_{5z} - e_{2x} + e_{5x} - e_{1x} + e_{4x})]$, $\xi^8 = 1/(2^{1/2})(2e_{4y} + 2e_{2y} - e_{1z} + e_{2z} + e_{4z} - e_{5z} - e_{1x} + e_{4x} + e_{2x} - e_{5x})$, $\xi^{10} = [e_{1x} + e_{2x} + e_{1z} + e_{4x} + e_{5x} + e_{4z} + e_{2z} + e_{5z}, -1/(2^{1/2})(-2e_{4y} - 2e_{2y} - e_{1z} + e_{2z}$ $+ e_{4z} - e_{5z} - e_{1x} + e_{4x} + e_{2x} - e_{5x})]$
25	***4(e):*** $\varphi^2 = 2(a_{1x} + a_{1y})$, $\xi_1{}^7 = 2(a_{1x} - a_{1y})$, $\xi_2{}^7 = 4a_{1z}$	***2(c), 2(d), 4(e):*** $\varphi^4 = 2(d_{1x} - d_{1y})$, $\varphi^2 = [2(d_{1x} + d_{1y}), 2(2^{1/2})d_{1z}]$	***4(e), 4(e), 4(e), 4(e):*** $\varphi^4 = (e_{1x} + e_{1y} - e_{2x} - e_{2y} + e_{7x} - e_{7y} - e_{8x} + e_{8y}, e_{1y} + e_{1x} - e_{2y} - e_{2x} - e_{8y} + e_{8x}$ $+ e_{7y} - e_{7x})$, $\varphi^2 = (e_{1x} + e_{2x} - e_{7x} - e_{8x} + e_{2y} + e_{1y} - e_{8y} - e_{7y}, e_{1y} + e_{2y} + e_{7y} + e_{8y} + e_{2x} + e_{1x}$ $+ e_{8x} + e_{7x}, 2e_{7z} - 2e_{8z})$ $\xi^1 = -2/(3^{1/2})(-e_{7x} - e_{7y} - e_{7z} + e_{8x} + e_{8y} - e_{8z} + e_{1y} - e_{1x} + e_{2z} + e_{1z} + e_{2x} - e_{2y})$, $\xi^5 = 1/(3^{1/2})(-e_{2x} + 2e_{1z} - 2e_{8z} + e_{1x} - e_{8y} + 2e_{2z} + e_{2y} - 2e_{7z} + e_{7x} - e_{1y} + e_{7y} - e_{8x})$, $\xi_1{}^7 = [e_{1x} + e_{2x} - e_{1y} - e_{2y} + e_{7x} + e_{8x} - e_{8y} - e_{7y}, 1/(2^{1/2})(-e_{8y} - e_{7y} + e_{2y} + e_{1y} - e_{1x}$ $- e_{2x} + 2e_{1z} - 2e_{2z} + e_{7x} + e_{8x})]$, $\xi_2{}^7 = [2(e_{1z} + e_{2z} + e_{7z} + e_{8z}), (2^{1/2})(e_{8y} - e_{7y} + e_{2y} - e_{1y} - e_{7x} + e_{8x} + e_{1x} - e_{2x})]$, $\xi^9 = 1/(2^{1/2})(-e_{8y} - e_{7y} + e_{2y} + e_{1y} - e_{1x} - e_{2x} - 2e_{1z} + 2e_{2z} + e_{7x} + e_{8x})$

Table 2 (continued)

	Wyckoff position		
Phase	8*a*	16*d*	32*e*
26	***4(e):*** $\varphi^1 = 2(a_{1y} + a_{1z})$, $\varphi^2 = 2(a_{1y} - a_{1z})$, $\xi^7 = 4a_{1x}$	***2(b), 2(d), 4(e):*** $\varphi^1 = 2(d_{1y} + d_{1z})$, $\varphi^2 = [2(d_{1y} - d_{1z}), -2(2^{1/2})d_{1x}]$	***4(e), 4(e), 4(e), 4(e):*** $\varphi^1 = [e_{1y} - e_{2y} + e_{3z} - e_{4z} + e_{1z} - e_{2z} - e_{4y} + e_{3y}, -e_{1z} - e_{2z} - e_{3y} - e_{4y} - e_{1y} - e_{2y}$ $- e_{4z} - e_{3z}, 2(e_{1x} + e_{3x})]$, $\varphi^2 = [e_{1y} - e_{2y} - e_{3z} + e_{4z} - e_{1z} + e_{2z} - e_{4y} + e_{3y}, -e_{1z} - e_{2z} + e_{3y} + e_{4y} + e_{1y} + e_{2y}$ $- e_{4z} - e_{3z}, 2(-e_{2x} - e_{4x})]$, $\xi^1 = 2/(3^{1/2})(-e_{1z} + e_{1x} - e_{1y} - e_{2x} - e_{2z} - e_{3x} + e_{3y} + e_{3z} + e_{4x} - e_{4y} + e_{4z} + e_{2y})$, ${\xi_1}^5 = [-1 + 1/(3^{1/2})][-e_{4y} + e_{4z} - 2e_{1x} + e_{2y} - e_{2z} + 2e_{3x} + e_{3y} + e_{3z} - 2e_{4x} - e_{1y} + 2e_{2x}$ $- e_{1z} + (3^{1/2})(e_{4z} - e_{1x} - e_{2z} + e_{3x} + e_{3z} - e_{4x} + e_{2x} - e_{1z})]$, ${\xi_2}^5 = -1/(3^{1/2})[2e_{2z} - e_{3x} + e_{3y} - 2e_{3z} + e_{4x} - e_{1y} - e_{2x} + 2e_{1z} - e_{4y} - 2e_{4z} + e_{2y} + e_{1x}$ $+ (3^{1/2})(e_{3x} + e_{3y} - e_{4x} - e_{1y} + e_{2x} - e_{4y} + e_{2y} - e_{1x})]$, $\xi^7 = [2e_{1x} + 2e_{2x} - 2e_{3x} - 2e_{4x}, (2^{1/2})(-e_{2z} + e_{1z} + e_{4z} - e_{3z} + e_{1y} + e_{2y} - e_{4y} - e_{3y})]$, $\xi^9 = (2^{1/2})(e_{2z} - e_{1z} - e_{4z} + e_{3z} + e_{1y} + e_{2y} - e_{4y} - e_{3y})$
27	***4(a):*** $\varphi^1 = 4a_{1z}$, $\varphi^2 = 4a_{1y}$	***4(a), 4(a):*** $\varphi^1 = 2(d_{1y} + d_{1z} - d_{5y} - d_{5z})$, $\varphi^2 = [2(d_{1y} - d_{1z} - d_{5y} + d_{5z})$, $2(2^{1/2})(-d_{1x} + d_{5x})]$, $\xi^6 = -[1 + (3^{1/2})]/(2^{1/2})(d_{1y}$ $+ d_{1z} + d_{5y} + d_{5z})$, $\xi^{10} = [2(2^{1/2})(d_{1x} + d_{5x})$, $2(d_{1y} - d_{1z} + d_{5y} + d_{5z})]$	***4(a), 4(a), 4(a), 4(a):*** $\varphi^1 = [2(e_{1z} - e_{2z} - e_{4y} - e_{5y}), 2(-e_{1y} - e_{2y} - e_{4z} + e_{5z}), 2(e_{1x} + e_{2x} - e_{4x} - e_{5x})]$, $\varphi^2 = [2(e_{1y} - e_{2y} + e_{4z} + e_{5z}), 2(-e_{1z} - e_{2z} + e_{4y} - e_{5y}), 2(e_{1x} - e_{2x} - e_{4x} + e_{5x})]$, $\xi^1 = 2/(3^{1/2})(e_{5z} + e_{5y} - e_{5x} + e_{4z} - e_{4y} + e_{4x} - e_{2z} + e_{2y} - e_{2x} - e_{1z} - e_{1y} + e_{1x})$, $\xi^5 = -[1 + 1/(3^{1/2})]/2(-e_{2z} + e_{2y} - 2e_{4x} + e_{5y} + e_{5z} - e_{1y} + 2e_{2x} - e_{1z} - e_{4y}$ $+ 2e_{5x} + e_{4z} - 2e_{1x})$, $\xi^6 = -[1 + 1/(3^{1/2})]/2(e_{5z} - e_{1y} - e_{5y} + e_{4y} + e_{4z} + e_{1z} + e_{2z} + e_{2y})$, $\xi^9 = -(2^{1/2})(-e_{1y} + e_{1z} - e_{2y} - e_{2z} + e_{4y} + e_{4z} + e_{5y} - e_{5z})$, $\xi^{10} = [2e_{1x} + 2e_{2x} + 2e_{4x} + 2e_{5x}, (2^{1/2})(e_{1y} + e_{1z} + e_{2y} - e_{2z} + e_{4y} - e_{4z} + e_{5y} + e_{5z})]$
28	***4(a):*** $\varphi^2 = 2(-a_{1x} + a_{1z})$, $\xi^7 = a_{1y}$, $\xi^{10} = 2(a_{1x} + a_{1z})$	***4(a), 4(a):*** $\varphi^4 = 2(d_{3x} - d_{3z})$, $\varphi^2 = [2(d_{1x} - d_{1z}), -2(2^{1/2})d_{1y}]$, $\xi^8 = d_{1x} - d_{1z} - d_{3x} - 2d_{3y} - d_{3z}$, $\xi^{10} = [(2^{1/2})(d_{1x} + d_{1z} + d_{3x} + d_{3z})$, $- d_{1x} - d_{1z} + d_{3x} - 2d_{3y} + d_{3z}]$	***4(a), 4(a), 4(a), 4(a):*** $\varphi^4 = (e_{1x} + e_{1z} - e_{2x} + e_{2z} - e_{4z} + e_{4x} - e_{3x} - e_{3z}, - e_{3x} - e_{3z} - e_{4x} + e_{4z} + e_{1z}$ $+ e_{1x} - e_{2z} + e_{2x})$, $\varphi^2 = [-e_{1z} + e_{2z} + e_{3x} - e_{4x} + e_{4z} - e_{3z} + e_{1x} - e_{2x}, -e_{1x} - e_{2x} + e_{3z} + e_{4z} - e_{4x}$ $- e_{3x} + e_{1z} + e_{2z}, 2(e_{1y} + e_{3y})]$, $\xi^8 = 1/(2^{1/2})(e_{4x} - e_{1x} + e_{4z} + 2e_{4y} - e_{3z} + e_{2z} + 2e_{2y} - e_{1z} - e_{3x} + e_{2x})$, $\xi^1 = 2/(3^{1/2})(-e_{1z} + e_{1x} - e_{1y} - e_{2x} - e_{2z} - e_{3x} + e_{3y} + e_{3z} + e_{4x} - e_{4y} + e_{4z} + e_{2y})$, $\xi^5 = [-1 + 1/(3^{1/2})]/2(-e_{4x} + e_{2x} + e_{2z} - 2e_{1y} + 2e_{2y} + 2e_{3y} - 2e_{4y} - e_{1x} + e_{3x}$ $- e_{3z} + e_{1z} - e_{4z})$, $\xi^7 = [2(e_{1y} + e_{2y} - e_{3y} - e_{4y}), 1/(2^{1/2})(-e_{4x} + e_{1x} - e_{4z} + e_{3z} + e_{2z} - e_{1z} - e_{3x} + e_{2x})]$, $\xi^{10} = [e_{1x} + e_{2x} + e_{3x} + e_{4x} + e_{1z} + e_{4z} + e_{2z} + e_{3z}, -1/(2^{1/2})(e_{4x} - e_{1x} + e_{4z} - 2e_{4y} - e_{3z}$ $+ e_{2z} - 2e_{2y} - e_{1z} - e_{3x} + e_{2x})]$

The OPs associated with the representations of equation (4) will always result in an ordering of octahedra. According to the chosen mechanism it must not exist, so it should be excluded from the set of OPs [equation (3)] contained in the composition of equation (4). Finally, a set of OPs for structures of the octahedra rotation is as follows:

$$\mathbf{k}_9(\tau_2 + \tau_3 + \tau_6) + \mathbf{k}_{10}(\tau_2 + \tau_4) + \mathbf{k}_{11}(\tau_5 + \tau_9). \qquad (5)$$

IRs $\mathbf{k}_9$: τ_2 are four dimensional; $\mathbf{k}_9$: τ_6 eight dimensional; $\mathbf{k}_{10}$: τ_2, τ_4 six dimensional; $\mathbf{k}_{11}$: τ_5 two dimensional; $\mathbf{k}_{11}$: τ_9 three dimensional. Thus, the overall dimension of the OP is 33. The full list of low-symmetry distortions for the OPs [equation (5)] contains 134 low-symmetrical phases. Of these, only five satisfy the selected criteria. The OPs for these phases are shown in Table 3. All phases are identified by only one OP.

The connection of the OP for the obtained low-symmetry phase caused by octahedra rotation with the displacements of spinel atoms is given in Table 4.

4. Discussion of the results

It is seen from the analysis of Table 3 that phase numbers 1 and 2 have no improper OPs. Therefore we can call these phases pure tilting phases. The structures of these phases are formed from the spinel structure by the particular oxygen displacements that cause octahedra rotation. There are no other displacements of oxygen atoms in these structures. Phase number 3 (Table 3) has improper OP $\boldsymbol{\tau}_5$ (k_{11}). This representation is part of the composition of the representation of equation (5), characterizing octahedral rotation. Therefore this phase can be considered as the phase of pure octahedra rotation too.

For the same reason phase number 17 (Table 1) is the phase of pure rotation: it has no improper OP. This phase is the phase of pure tetrahedra rotation.

In all other phases there are improper OPs that do not characterize only rotation of polyhedra (tetrahedra and octahedra). The phases of pure rotation in Tables 1 and 3 are given in bold.

The most widespread phase transition in the spinel family associated with rotation of tetrahedra is transformation with the change of space groups $Fd\bar{3}m \rightarrow P4_332$ (or enantiomorphic to this group a group with symmetry $P4_132$). This transformation is induced by a six-dimensional IR $\mathbf{k}_{10}$: τ_1 (Sahnenko *et al.*, 1982, 1983, 1986). The six-component OP has the form (φ, 0, $-\varphi$, 0, $-\varphi$, 0) (see Table 1).

Critical IR $\mathbf{k}_{10}$: τ_1 enters permutational (at Wyckoff positions 16*d* and 32*e*) and mechanical (Wyckoff positions 8*a*, 16*d*, 32*e*) representations of the crystal. Therefore, lowering of the crystal symmetry is due to ordering of the octahedral cations and anions and displacements of all types of atoms in cubic spinel (Sahnenko *et al.*, 1983). Calculations show that simul-

Table 3
Low-symmetry phases formed by octahedra tilting in the spinel structure.

Designations for OPs: $\mathbf{k}_{10} - \varphi$, $\mathbf{k}_{11} - \xi$. The superscript index after the closing parenthesis is the representation number according to Kovalev (1965, 1993); $\varepsilon = [2 + (3^{1/2})]$. V'/V is the change of primitive cell volume as a result of structural phase transition. The phases of pure tilting are given in bold.

Phase	OP	Improper OP	Symbol of space group	V'/V	Translations of primitive cell of the $Fd\bar{3}m$ structure
1	$\boldsymbol{(\xi, \varepsilon\xi)^5}$		$I4_1/amd$ (No. 141)	1	$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$
2	$\boldsymbol{(\xi_1, \xi_2)^5}$		$Fddd$ (No. 70)	1	$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$
3	$\boldsymbol{(0, \xi, 0)^9}$	$(\xi, \varepsilon\xi)^5$	$I4_1/a$ (No. 88)	1	$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$
4	$(0, 0, \varphi, 0, 0, 0)^4$	$(\xi)^4$ $(\xi, \varepsilon\xi)^5$ $(\varepsilon\xi, \xi)^6$	$P\bar{4}n2$ (No. 118)	2	$\mathbf{a}_1 + \mathbf{a}_3, \mathbf{a}_2, 2\mathbf{a}_3$
5	$(0, 0, \varphi, 0, 0, 0)^2$	$(\xi, \varepsilon\xi)^5$ $(\xi, \varepsilon\xi)^6$	$P4_12_12$ (No. 92), $P4_32_12$ (No. 96)	2	$\mathbf{a}_1 + \mathbf{a}_3, \mathbf{a}_2, 2\mathbf{a}_3$

Table 4
Connection of order parameters with atom displacements in octahedra rotation structures.

Designations in Table 4 are the same as in Table 2.

Phase	Wyckoff position		
	8*a*	16*d*	32*e*
1	***4(a)***	***8(d)***	***16(h):*** $\xi^5 = 4[1 - 1/(3^{1/2})](e_{1x} + e_{1y})$, $\xi^1 = 8/(3^{1/2})(2e_{1x} - e_{1y})$
2	***8(a)***	***16(d)***	***32(h):*** ${\xi_1}^5 = 4/(3^{1/2})[2e_{1z} + e_{1x} - e_{1y} + (3^{1/2})(e_{1x} + e_{1y})]$, ${\xi_2}^5 = -4/(3^{1/2})[2e_{1z} + e_{1x} - e_{1y} - (3^{1/2})(e_{1x} + e_{1y})]$, $\xi^1 = 8/(3^{1/2})(e_{1x} - e_{1y} - e_{1z})$
3	***4(a)***	***8(d)***	***16(f):*** $\xi^9 = 4(2^{1/2})(2e_{1x} + e_{1z})$, $\xi^1 = 8/(3^{1/2})(e_{1x} - e_{1y} - e_{1z})$, $\xi^5 = 2[-1 + 1/(3^{1/2})](-e_{1x} - 2e_{1y} + e_{1z})$
4	***2(a), 2(d)***	***8(i):*** $\varphi^4 = -4(d_{1x} + d_{1z})$, $\xi^4 = 4(2/3)^{1/2}(d_{1x} + d_{1y} - d_{1z})$, $\xi^6 = [1 + (3^{1/2})]/(2^{1/2})(d_{1x} - 2d_{1y} - d_{1z})$	***8(i), 8(i):*** $\varphi^4 = [4(e_{1x} + e_{1z}), -4(e_{3x} + e_{3z})]$, $\xi^1 = 4/(3^{1/2})(e_{1x} - e_{1y} - e_{1z} - e_{3x} + e_{3y} + e_{3z})$, $\xi^4 = 4/(3^{1/2})(e_{1x} - e_{1y} - e_{1z} + e_{3x} - e_{3y} - e_{3z})$, $\xi^5 = [-1 + 1/(3^{1/2})](2e_{3y} - 2e_{1y} + e_{1z} - e_{1x} - e_{3z} + e_{3x})$, $\xi^6 = -[1 + 1/(3^{1/2})](-e_{1x} + e_{1z} - e_{3x} + e_{3z} - 2e_{1y} - 2e_{3y})$
5	***4(a):*** $\varphi^2 = 4a_{1z}$	***8(b):*** $\varphi^2 = [4(d_{1x} - d_{1z}), -4(2^{1/2})d_{1y}]$, $\xi^6 = [1 - (3^{1/2})]/(2^{1/2})(d_{1x} + d_{1z})$	***8(b), 8(b):*** $\varphi^2 = [4(-e_{1z} + e_{2z}), -4(e_{1x} + e_{2x}), 4(e_{1y} + e_{2y})]$, $\xi^1 = 4/(3^{1/2})(e_{1x} - e_{1y} - e_{1z} - e_{2x} + e_{2y} - e_{2z})$, $\xi^5 = [-1 + 1/(3^{1/2})](e_{2x} - e_{1x} + e_{2z} + e_{1z} - 2e_{1y} + 2e_{2y})$, $\xi^6 = [1 - (3^{1/2})](e_{1z} + e_{1x} - e_{2x} + e_{2z})$

taneously with the ordering of the cations in the octahedral sublattice (type 1:3) anion ordering occurs (Talanov, 1990, 1996*a*,*b*, 2007). When forming an ordered phase, the displacement of tetrahedral and octahedral cations and also anions takes place. Found by calculation, the sites which occupy the tetrahedral *A* cations, the octahedral *B* cations and anions *X* in the ordered spinel – $A_2^{8c}B^{4b}B_3^{12d}X_2^{8c}X_6^{24e}$ – are consistent with the data of X-ray and neutron diffraction studies (Table 5) (Joubert & Durif, 1964; Vandenberghe *et al.*, 1976; Dargel & Wolinski, 1976; Van der Biest & Thomas, 1975; Talanov, 1989*a*). The calculated structure of the ordered phase is shown in Figs. 2 and 3. Since some of the sites contain free parameters, then, depending on the signs and magnitudes of these parameters, the existence of different isostructural modifications of ordered structure is possible. Low-symmetry phases, for example, $LiAl_5O_8$ and $Cu_{3/2}Mn_{3/2}O_4$, belong to different isostructural modifications of ordered spinel (Talanov, 1990).

The qualitative character of the rotation of the tetrahedra is shown in Fig. 3. In this figure ordering structure (structure with the rotation of the tetrahedra) is compared with the structure of the ideal spinel structure with two types of anions, placed in the same way as in the ordering spinel structure (Figs. 3*a*, 3*b*, 3*c*, 3*d*).

An interesting symmetrical feature of the ordered phase structure formed by the rotation of the tetrahedra is that, among the elements of symmetry of the space group of the phase structure, there are no inversion symmetry planes, only the symmetry axes. Such crystals may exist as the right- and left-hand forms. They are mirror images of each other. The phases with the symmetry of $P4_332$ and $P4_132$, which are enantiomorphous modifications, are indistinguishable (except for optical activity) by the physical properties. In crystals of lithium ferrite $LiFe_5O_8$ they exist in the same sample as domains (Talanov, 1996*a*,*b*).

The most widespread phase transition in the spinel family associated with pure rotation of octahedra is that induced by the two-dimensional IR of wavevector $\mathbf{k}_{11}$: τ_5 (Sahnenko *et al.*, 1982, 1983, 1986). An ordered arrangement of distorted octahedra and tetrahedra causes a tetragonal or orthorhombic crystal structure as a whole (space group $I4_1/amd$ or $Fddd$).

Table 5
Structural identification of phase states.

The number and multiplicity (in parentheses) of the Wyckoff position are indicated. After the colon the local symmetry of the Wyckoff position is given. For example, the record of 1(8): $3(C_3)$ + 1(24): $1(C_1)$ means that Wyckoff position 32e of group $Fd\bar{3}m$ in the low-symmetry phase G_D with space group $P4_332$ (O^6) or $P4_132$ (O^7) stratified into one eightfold Wyckoff position with local symmetry $3(C_3)$ and one 24-fold Wyckoff position with local symmetry $1(C_1)$. $\varepsilon = [2 + (3^{1/2})]$.

			Stratification of Wyckoff position		
OP	IR	G_D	8a	16d	32e
$(\varphi, 0, -\varphi, 0, -\varphi, 0)$	$\mathbf{k}_{10}$: τ_1	$P4_332$ or $P4_132$	1(8): $3(C_3)$	1(4): $32(D_3)$ + 1(12): $2(C_2)$	1(8): $3(C_3)$ + 1(24): $1(C_1)$
$(\xi, \varepsilon\xi)$	$\mathbf{k}_{11}$: τ_5	$I4_1/amd$	1(4): $\bar{4}m2(D_{2d})$	1(8): $2/m(C_{2h})$	1(16): $m(C_s)$
(ξ_1, ξ_2)	$\mathbf{k}_{11}$: τ_5	$Fddd$	1(8): $222(D_2)$	1(16): $\bar{1}(C_i)$	1(32): $1(C_1)$

Therefore the chain of transitions ($Fd\bar{3}m \to I4_1/amd \to Fddd$) is possible.

Note the structural features of the tetragonal and orthorhombic structures of deformed spinel induced by rotation of the octahedra. IR $\boldsymbol{\tau}_5$ of vector $\mathbf{k}_{11}$ enters the composition of a mechanical representation on Wyckoff positions 32e. Consequently, these structural transitions are of the displacement type. A detailed theoretical structural study of the mechanisms of forming the tetragonal and orthorhombic phases was carried out earlier (Talanov, 1989a; Ivanov & Talanov, 1995a,b). Note that in the tetragonal phase the anions occupy divariant Wyckoff position 16h with a monoclinic local symmetry m; tetrahedral and octahedral cations occupy, respectively, nonvariant Wyckoff positions 4a (the site symmetry at position 4a is $\bar{4}m2$) and 8d (the site symmetry at position 8d is $2/m$) (Figs. 4, 5 and 6, Table 5).

The displacement of the anions in the unit cell of the spinel structure is shown in Fig. 5, leading to the formation of the tetragonal phase $c/a > 1$ (see Figs. 5a,b) and tetragonal phase with $c/a < 1$ (see Figs. 5c,d). The direction of displacement of the anions in the octahedra by x and y coordinates coincides with the displacements of the anions in the cubic spinel and is opposite on the coordinate z: displacements of the anions, leading to the formation of a tetragonally elongated phase $c/a > 1$, are directed not to the 'inside' of the hexahedron (the cube B_4O_4), but to the 'outside' (Fig. 5). It leads to formation of tetragonally elongated octahedra. In the formation of the tetragonal shortened phase with $c/a < 1$ the displacements of the anions are of the opposite sign. The anion displacements have a specific character; they have led to rotation of octahedra. Octahedra have bent as shown in Figs. 6(a), 6(d) and 6(c), 6(f).

In distorted octahedra there are two interionic distances that are unequal to each other, 'octahedral cation–anion', and six non-equivalent 'anion–anion' distances. The displacements of the anions in a tetrahedron are such that all four interionic distances $(A-X)_4$ are equal; only the $X-A-X$ angles change.

These results of the analysis of the tetragonal structure features are confirmed by numerous experimental facts. For example, in $NiCr_2O_4$ [c/a = 1.04 (Krupichka, 1976)] and $NiRh_2O_4$ [c/a = 1.04 (Krupichka, 1976)] lattice distortion is due to the tetrahedral coordinated ions of Ni^{2+}. It was established experimentally that the four distances $(Ni^{2+}-O)_4$ in tetrahedra are equal to each other, while the O—Ni—O angles deviate from their ideal values (Muller & Roy, 1974).

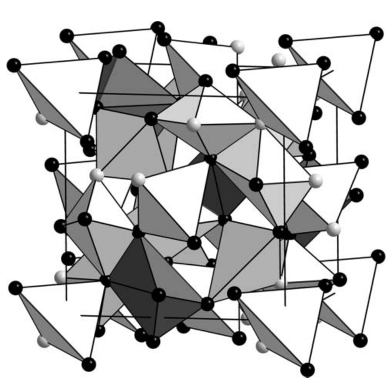

Figure 2
Calculated polyhedral model of the ordered spinel modification (the structure of the pure rotation of the tetrahedra) with space group $P4_332$. Octahedra around the atom B^{4b} are dark, around the atom B^{12d} are light; tetrahedra around the atom A^{8c} are light.

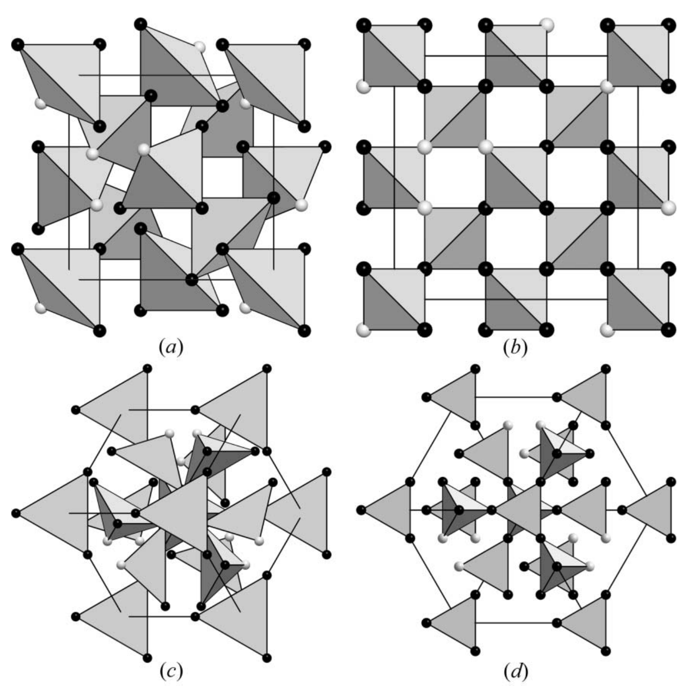

Figure 3
Projections (001) and (111) of structures of the ordered spinel modification with space group $P4_332$ (a), (c), and ideal spinel (b), (d) (octahedra not shown). Black circles represent oxygen atoms in positions 24e, light circles represent oxygen atoms in position 8c of the $P4_332$ phase.

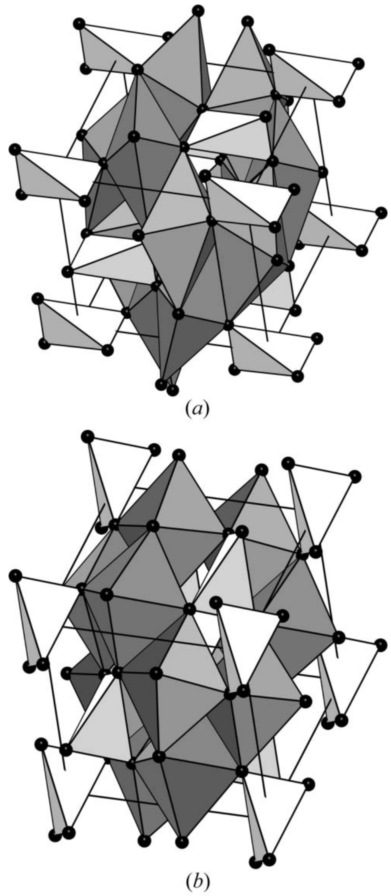

Figure 4
Calculated qualitative picture of the fragment of the distorted spinel structure with the space group $I4_1/amd$ (in the basis of the spinel cubic lattice): (*a*) the structure of the phase with the degree of tetragonality c/a = 1.03, (*b*) the structure of the phase with the degree of tetragonality c/a = 0.97. The magnitudes of the free parameters of oxygen (y, z) are taken to show clearly the character of tetrahedra and octahedra distortions in tetragonal spinel modifications. The two elementary cells have the same orientations.

The oxygen octahedron with a chromium ion in the centre is highly distorted. There are two different distances $(Cr^{3+}{-}O)_6$ equal to 0.198 and 0.199 nm (Ivanov & Talanov, 1995*b*). Similar experimental data obtained for other crystals (for Mn spinels, see Nogues & Poix, 1974, 1972) confirm the proposed mechanism of tetragonal distortion of the spinel.

It is of interest that the formation of a tetragonally elongated tetrahedron leads to the formation of a tetragonal shortened octahedron (Fig. 4*b*), and formation of a tetragonally shortened tetrahedron is accompanied by the formation of a tetragonally elongated octahedron (Fig. 4*a*). Krupichka (1976) reports an investigation of spinel systems containing Jahn–Teller ions in tetrahedral and octahedral positions. It is noted that Cu^{2+} ions in tetrahedral positions have a compensating effect on the distortion caused by the Cu^{2+} and Mn^{3+} ions in the octahedral positions. Krupichka believes that this effect is a consequence of the opposite distorting influence – tetrahedral Cu^{2+} ions 'prefer' the type of distortion $c/a < 1$, while the octahedral Cu^{2+} and Mn^{3+} ions prefer distortions with $c/a > 1$. We emphasize that from the examined mechanism of phase transition the compensation effect follows naturally (the opposite character of the distortion of the tetrahedron and octahedron); it exists even in the situation where there is only one kind of Jahn–Teller ion in one type of position.

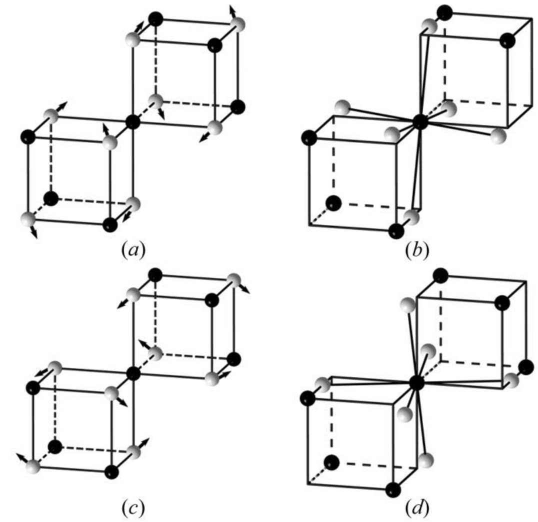

Figure 5
The displacements of the anions in the octahedron BX_6 (*a*), (*c*). Distorted octahedron (*b*), (*d*).

It is also interesting to note that the ordered arrangement of elongated (shortened) octahedra is not a 'pure' ordering of the 'ferro' type. The axes of elongated (shortened) octahedra and tetrahedra are parallel to each other in the case of 'ferro'-type ordering (similar to parallel orientation of magnetic moments in ferromagnetics). The tilting of the octahedra leads to deviation from a parallel orientation of elongated (shortened) octahedra. The orientation of distorted octahedra is shown in Figs. 4 and 6.

In the formation of the orthorhombic phase the rotation of the octahedra leads to the *A* cations occupying, as in the cubic spinel, Wyckoff position 8*a*, but with local symmetry 222. *B* cations in the structure of the orthorhombic phase are in Wyckoff position 16*d* with local symmetry $\overline{1}$, and the anions occupy general Wyckoff position 32*h* with local symmetry 1 (Fig. 7 and Table 5). Apparently, according to this mechanism, solid solutions $CuFe_{2-x}Al_xO_4$ ($0.04 < x < 0.45$) and spinel $Cu_{1,2}Ge_{0,2}Fe_{1,6}O_4$ are formed (Antoshkin *et al.*, 1985; Belov *et al.*, 1983).

Distortions of the octahedra and tetrahedra in the orthorhombic phase are more various than in the tetragonal phase. This is connected with the fact that the oxygen-atom position in the tetragonal structure is defined by two parameters x_t and z_t. The values of these parameters are expressed by the spinel oxygen parameter $u \simeq 3/8$ and the oxygen-atom displacement x_{an} according to the following formulas: $x_t = -2(u + x_{an})$; $z_t = u + x_{an}$. Rough estimation of x_t and z_t gives $x_t \simeq 1/4$, $z_t \simeq 3/8$ (Talanov, 1989*b*).

Oxygen-atom positions in the orthorhombic structure are defined by three parameters which depend on the spinel oxygen parameter and two parameters of the theory. Theo-

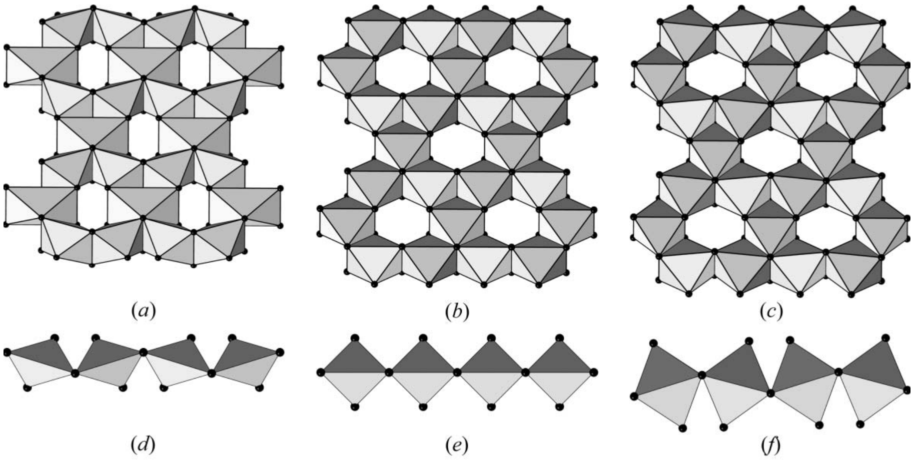

Figure 6
Projection (111) of the distorted (*a*), (*c*) and undistorted (*b*) structure of spinel (only octahedra are shown), fragments of octahedral chains (*d*), (*e*), (*f*) in tetragonal spinel modifications: $c/a > 1$ (*a*), (*d*); $c/a = 1$ (*b*), (*e*); $c/a < 1$ (*c*), (*f*).

retical calculations of the structural mechanism of *Fddd* phase formation show the possibility of the existence of isosymmetric modifications of the orthorhombic phase (Ivanov & Talanov, 1995*a*). These phases differ from one another by the values of the free parameters *x*, *y* and *z*, which define the oxygen position in an elementary cell. Examples of two calculated structures of the *Fddd* phase are shown in Fig. 7.

Thus, in this paper for the first time the structure rotation in spinels has been studied by the methods of group-theoretical analysis of phase transitions. It is shown that there are 28 phases of rotation of the tetrahedra and five phases of octahedra rotation. It is established that among the possible phases of rotation of the tetrahedra there is one phase of pure tetrahedra rotation. It is also shown that out of the five phases of octahedra rotation there are only three phases of pure octahedra rotation. Comparison of the theoretical prediction of the possible phases of rotation with the results of modelling of the structure of some widespread types of low-symmetry modifications of spinel has been made. The specific features of their structure have been found.

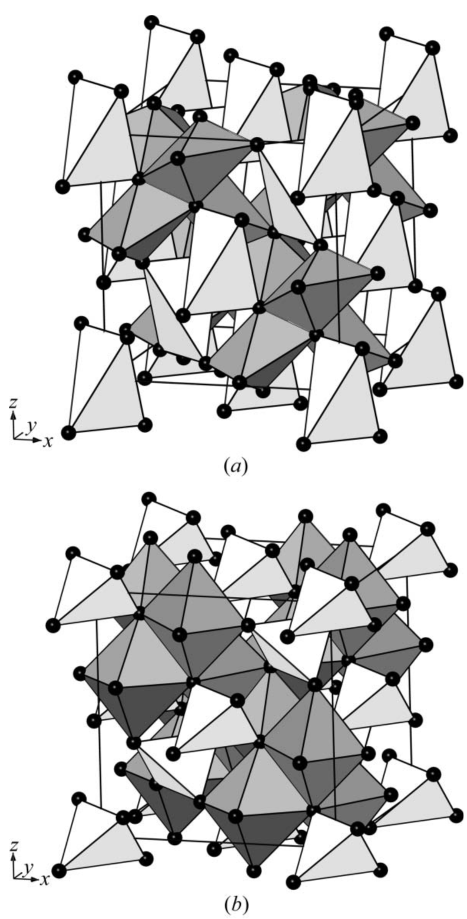

Figure 7
A qualitative picture of the distorted spinel structure of the fragment with the space group *Fddd* (in the basis of the spinel cubic lattice): (*a*) $x = 0.38$, $y = 0.35$, $z = 0.45$; (*b*) $x = 0.39$, $y = 0.39$, $z = 0.365$; *x*, *y*, *z* – free parameters of the *Fddd* phase structure. The magnitudes of the free parameters of oxygen (*x*, *y*, *z*) are taken to show vividly the character of the tetrahedra and octahedra distortions in orthorhombic spinel modifications. The elementary cells in (*a*) and (*b*) have the same orientation.

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