

Atomic order in the spinel structure – a group-theoretical analysis

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Group-theoretical methods of the Landau theory of phase transitions are used to investigate the structures of ordered spinels. The possibility of the existence is determined of 305 phases with different types of order in Wyckoff position $8a$ (including seven binary and seven ternary cation substructures), 537 phases in Wyckoff position $16d$ (including eight binary and 11 ternary cation substructures), 595 phases in Wyckoff position $32e$ (including seven binary and four ternary anion substructures) and 549 phases with simultaneous ordering in Wyckoff positions $8a$ and $16d$ (including five substructures with binary order in tetrahedral and octahedral sublattices, two substructures with ternary order in both spinel sublattices, and nine substructures with different combined types of binary and ternary order). Theoretical results and experimental data are compared. Calculated structures of the spread types of ordered low-symmetry spinel modifications are given.

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1. Introduction

The spinel structure was discovered independently by Bragg (1915) and Nishikawa (1915) almost a century ago. At present, substances with this structure are of great interest for a wide community of chemists, physicists, mineralogists, metallurgists and specialists in material science. Initially, spinel applications were based on their magnetic and electric properties (Krupichka, 1976; Talanov, 1986a). Later their other unique physical properties were discovered. It was revealed that among spinels there were superconductors (LiTi_2O_4 , CuRh_2S_4 , CuV_2S_4 , CuRh_2Se_4) (Johnston *et al.*, 1973; Robbins *et al.*, 1967), crystals with superionic conductivity (Li_2MCl_4 , where $M = \text{Mg, V, Mn, Fe, Cd}$, bromide spinels and others) (Kanno *et al.*, 1981; Lutz *et al.*, 1985, 1997; Schmidt & Lutz, 1984), numerous materials for electrodes in chemical current sources (Thackeray, 1997; Ezikian *et al.*, 1988; Talanov *et al.*, 2007) and multiferroics (CoCr_2O_4) (Ederer & Spaldin, 2004; Yamasaki *et al.*, 2006; Torgashev *et al.*, 2012; Pollert, 1988; Gorjaga *et al.*, 1990). Some spinels are used in the production of ceramic materials, fireproofs and thermoresistant dyes (Krupichka, 1976; Pollert, 1988; Gorjaga *et al.*, 1990). Most of these spinel properties depend largely on atomic ordering. Let us explain this idea.

The general chemical formula of the spinels is AB_2X_4 . The spinel structure has the space group $Fd\bar{3}m$. It represents the closest cubic threefold layer packing of X atoms. The elementary spinel cell consists of eight cations which occupy Wyckoff position $8a$, 16 cations in Wyckoff position $16d$, and 32 anions X in Wyckoff position $32e$. The cation distribution on the nonequivalent crystallographic positions $8a$ and $16d$

can be described by the formula $(A_\lambda B_{1-\lambda})^{8a}[A_{1-\lambda} B_{1+\lambda}]^{16d} X_4$, where λ is the so-called degree of inversibility of the spinel structure. The parameter λ depends on the chemical nature of the substance and the conditions of spinel preparation, temperature and pressure. In more complicated spinels containing certain types of cations, it is necessary to introduce more parameters of the λ type to describe the structure.

With changing the temperature (T), the concentration of solid solution (x) or the pressure (P), phase transitions can occur that are accompanied by cation redistribution and reorganization of the spinel structure. Four types of spinel structure reorganizations are possible.

(i) *Isostructural transitions*. The degree of inversibility of the spinel structure λ changes by jumping, but the crystal symmetry and its structural type do not change. In this case, the structural transformation is connected with cation redistribution among the nonequivalent crystallographic positions $8a$ and $16d$. The order parameter of this isosymmetrical and isostructural transition is $\lambda = \lambda(T, x, P)$. The isostructural transition theory for spinels was first proposed by Talanov & Bezrukov (1985, 1990). A general theory of isostructural transitions for different classes of crystals was developed by Talanov & Bezrukov (1986a,b) and Talanov *et al.* (1989).

(ii) *Reconstructive transitions*. At a reconstructive phase transition fundamental structural reorganization takes place (Toledano & Dmitriev, 1996). Examples of reconstructive phase transitions are spinel–olivine, spinel–phenacite and other transitions.

(iii) *Phase transitions of the second order*. In this case, continuous change of the spinel structure and its thermodynamic states, caused by atomic displacements and atomic

redistribution on Wyckoff positions, takes place (Landau & Lifshitz, 1980; Gufan, 1982; Toledano & Toledano, 1987). There are limiting group–subgroup relationships for these transitions.

(iv) *Phase transitions of the first order close to the second order.* At such structural transitions the thermodynamic state changes by jumping (and therefore they are phase transitions of the first order), but fundamental spinel structural transformation does not occur (Gufan, 1982). There are limiting group–subgroup relationships for these transitions too.

In this article we will consider possible types of atom ordering (possible superstructures) in spinel structures. By definition, a superstructure cannot be formed as a result of an isostructural transition. The remaining three mechanisms can lead to superstructure formation. We will limit our analysis to the third and fourth types of spinel structure reorganization.

The problem of finding possible superstructures is of great scientific and practical interest. Superstructure formation is accompanied by the appearance of new physical properties in a substance. For example, cation ordering is accompanied by new sublattice formation. This enables ferrimagnetism (Krupichka, 1976). An example is the spinel $\text{Cu}^+[\text{Ni}_{1/2}^{+2}\text{Mn}_{3/2}^{+4}]\text{O}_4$ with cation order in the octahedral positions (Krupichka, 1976). A low-temperature phase transition to an ordered magnetite phase is accompanied by an anomaly of the specific thermal capacity, conductivity and also a change of approximately two orders of magnitude of the magnetic crystallographic anisotropy (Gorjaga *et al.*, 1990). Abnormally high superionic conductivity is found in chloride spinels near the temperature of cation ordering (Kanno *et al.*, 1981, 1986, 1987; Lutz *et al.*, 1985, 1997; Schmidt & Lutz, 1984; Wussow *et al.*, 1989).

Enumeration of the possible superstructures for simple lattices has been carried out previously in various model approximations (Bragg–Williams; see, for example, Smirnov, 1966), a molecular field (see, for example, Vaks, 1973), static concentration waves (see, for example, Khachatryan, 1974), and also by a simple search of options of ‘colouring’ the positions of a crystal structure (Smirnova, 1956).

In contrast to these methods, which are limited to a number of coordination spheres, the type of interparticle interaction (pair, threefold *etc.*) and also a number of components of solid solution, we use a group-theoretical method of the thermodynamic theory of phase transitions. This method allows us to obtain the list of possible superstructures without applying any models.

The aim of this research is the full enumeration of all possible ordered structures of spinels. A group-theoretical approach has already been used for the study of some types of superstructures in spinels (Talanov, 1989, 1990*a,b*, 1996, 2007; Talanov & Chechin, 1990). In addition to these results, we considered secondary parameters of order and cases of simultaneous ordering in the two cation sublattices of the spinel structure. A peculiarity of the spinel structure is that cations of one type can be distributed between Wyckoff positions *8a* and *16d*. This means that an ordering description can demand two parameters of order. Such calculations have

not been carried out before. We also investigate possible superstructures in the *8a* and *16d* cation positions induced by irreducible representations of the wavevector κ_8 of $Fd\bar{3}m$ (this question has also not been considered before). In this work we will present a full picture of the possible types of atomic order in crystals with spinel structures.

The results of the calculations appear cumbersome, and therefore only part of the results will be given concerning binary and ternary cation and anion superstructures. These results may be of particular interest for experimental research.

2. Method of possible superstructure calculation

The group-theoretical method as a means of studying phase transitions of atom ordering in alloys was first proposed by Lifshitz (1941). This method was developed further by Gufan (1971, 1982), Kovalev (1993), Chechin (1989), Sahnenko *et al.* (1986) and Vinberg *et al.* (1974).

The structure of the low-symmetry ordered phase within Landau’s theory can be described by some function $\Delta\rho(r)$, for example, a function of the changing density of an electric charge:

$$\Delta\rho(r) = \rho(\mathbf{r}) - \rho_0(\mathbf{r}) = \sum_{i,n} c_i^{(n)} \varphi_i^{(n)}.$$

Here the index *n* is the number of the full irreducible representations (irreps) and the index *i* is the number of their basis functions $\varphi_i^{(n)}$. The coefficients $c_i^{(n)}$ are the components of order parameters; they depend on the thermodynamic conditions, in particular, on such variables as the pressure *P* and the temperature *T*: $c_i^{(n)} \sim c_i^{(n)}(P, T)$.

Based on the concept of one critical irrep, a large number of variables describing a crystal state is reduced to a small number of variables, being parameters of the order of the phase transformation. Therefore, the parameter of order selects those degrees of freedom according to which a crystal loses stability. The contribution from a critical irrep in $\rho(\mathbf{r})$ completely defines the symmetry of the low-symmetry (or dissymmetrical G_D) phase. However, when researching the G_D -phase structure far from the temperature of phase transition, the contribution of noncritical representations can become essential (Sahnenko *et al.*, 1986). Then the interpretation of some experimental data cannot be carried out only by means of a critical irrep. A method of finding noncritical atomic displacements and ordering is proposed (Sahnenko *et al.*, 1986).

In considering phase transitions of the ‘order–disorder’ type, it is convenient to use the scalar function φ defined on the given Wyckoff position and characterizing the ‘colours’ of positions appearing as a result of a phase transition. Identical $\Delta\rho(r)$ values have the same Wyckoff positions. Knowing the type of stratification of the Wyckoff positions of the initial phase structure with a symmetry of G_0 on the Wyckoff positions in the G_D -phase structure, it is possible to find the type of superstructure and the structural formula of the G_D phase (if we consider that on each Wyckoff position there is one type of atom).

Table 1

Binary and ternary cation ordering in Wyckoff position 8a of the spinel structure.

Designations for order parameters: $\mathbf{k}_8 - \theta$, $\mathbf{k}_9 - \eta$, $\mathbf{k}_{10} - \varphi$, $\mathbf{k}_{11} - \xi$. The superscript index after the closing parenthesis is the representation number according to Kovalev (1993) and V'/V is the change of primitive cell volume as a result of the structural phase transition. The superscript index in the structural formula means the type of Wyckoff position according to *International Tables for Crystallography*.

No.	Order parameters	Symbol of space group	V'/V	Translations of primitive cell of spinel structure	Structural formula
1	$(0, 0, 0, \varphi, \varphi, 0)^3$	$P4_22$ (No. 91) $P4_322$ (No. 95)	4	$\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3, 2\mathbf{a}_2, 2\mathbf{a}_3$	$A_{1/2}^{(a)} A_{1/2}^{(b)} B_{1/2}^{(c)} B_{1/2}^{(d)} B^{(d)} X^{(d)} X^{(d)} X^{(d)} X^{(d)}$
2	$(\xi)^4$	$F\bar{4}3m$ (No. 216)	1	$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$	$A_{1/2}^{(a)} A_{1/2}^{(d)} B_4^{(e)} X_4^{(e)} X_4^{(e)}$
3	$(\eta, 0, 0, 0)^4$	$R\bar{3}2/m$ (No. 166)	2	$\mathbf{a}_1 + \mathbf{a}_2, \mathbf{a}_1 + \mathbf{a}_3, 2\mathbf{a}_1$	$A_{1/2}^{(c)} A_{1/2}^{(c)} B_{1/4}^{(a)} B_{1/4}^{(b)} B_{3/2}^{(c)} X_{1/2}^{(c)} X_{1/2}^{(c)} X_{3/2}^{(h)} X_{3/2}^{(h)}$
4	$(\eta, 0, 0, 0)^1$	$R\bar{3}2/m$ (No. 166)	2	$\mathbf{a}_1 + \mathbf{a}_2, \mathbf{a}_1 + \mathbf{a}_3, 2\mathbf{a}_1$	$A_{1/2}^{(c)} A_{1/2}^{(c)} B_{1/2}^{(d)} B_{3/4}^{(e)} B_{3/4}^{(e)} X_{1/2}^{(c)} X_{1/2}^{(c)} X_{3/2}^{(h)} X_{3/2}^{(h)}$
5	$(0, 0, 0, 0, \varphi, \varphi)^3$	$Pcmm$ (No. 51)	2	$\mathbf{a}_2 + \mathbf{a}_3, \mathbf{a}_1, 2\mathbf{a}_2$	$A_{1/2}^{(e)} A_{1/2}^{(f)} B_{1/2}^{(b)} B_{1/2}^{(c)} B^{(k)} X^{(k)} X^{(k)} X^{(k)} X^{(k)}$
6	$(\varphi, -\varphi, -\varphi, -\varphi, -\varphi, \varphi)^3$	$R\bar{3}2/m$ (No. 166)	4	$\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3, 2\mathbf{a}_2, 2\mathbf{a}_3$	$A_{1/4}^{(c)} A_{3/4}^{(h)} B_{1/8}^{(d)} B_{3/8}^{(d)} B_{3/4}^{(f)} B_{3/4}^{(f)} X_{1/4}^{(c)} X_{3/4}^{(h)} X_{3/4}^{(h)} X_{3/2}^{(i)}$
7	$(0, \varphi, 0, 0, 0, 0)^3$ $(\xi)^4_{sec}$	$P\bar{4}m2$ (No. 115)	2	$\mathbf{a}_1 + \mathbf{a}_2, \mathbf{a}_3, 2\mathbf{a}_1$	$A_{1/4}^{(a)} A_{1/4}^{(c)} A_{1/2}^{(g)} B^{(i)} B^{(k)} X^{(i)} X^{(i)} X^{(k)} X^{(k)}$
8	$(0, \varphi, 0, \varphi, 0, -\varphi)^3$ $(\xi)^4_{sec}$	$P\bar{4}3m$ (No. 215)	4	$\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3, 2\mathbf{a}_2, 2\mathbf{a}_1$	$A_{1/8}^{(a)} A_{3/8}^{(c)} A_{1/2}^{(e)} B_{1/2}^{(e)} B_{3/2}^{(i)} X_{1/2}^{(e)} X_{1/2}^{(e)} X_{3/2}^{(i)} X_{3/2}^{(i)}$
9	$(\eta, \eta, 0, 0)^4$ $(0, 0, 0, 0, \varphi, -\varphi)^3_{sec}$	$Bbmm$ (No. 63)	4	$\mathbf{a}_2 + \mathbf{a}_3, 2\mathbf{a}_1, 2\mathbf{a}_2$	$A_{1/4}^{(c)} A_{1/4}^{(c)} A_{1/2}^{(g)} B_{1/2}^{(e)} B_{1/2}^{(g)} B_{1/2}^{(g)} X_{1/2}^{(f)} X_{1/2}^{(f)} X_{1/2}^{(g)} X_{1/2}^{(g)} X_{1/2}^{(g)} X_{1/2}^{(g)} X^{(h)}$
10	$(0, 0, \eta, \eta)^1$ $(0, 0, 0, 0, \varphi, \varphi)^3_{sec}$	$Ccmm$ (No. 63)	4	$\mathbf{a}_1, 2\mathbf{a}_2, 2\mathbf{a}_3$	$A_{1/4}^{(c)} A_{1/4}^{(c)} A_{1/2}^{(g)} B_{1/4}^{(b)} B_{1/4}^{(d)} B_{1/2}^{(g)} B_{1/2}^{(g)}$ $X_{1/2}^{(f)} X_{1/2}^{(f)} X_{1/2}^{(g)} X_{1/2}^{(g)} X_{1/2}^{(g)} X_{1/2}^{(g)}$
11	$(\varphi_1, -\varphi_1, \varphi_2, -\varphi_2, \varphi_2, \varphi_2)^3$	$C2/m$ (No. 12)	4	$\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3, 2\mathbf{a}_2, 2\mathbf{a}_3$	$A_{1/4}^{(i)} A_{1/4}^{(i)} A_{1/2}^{(j)} B_{1/8}^{(c)} B_{1/8}^{(d)} B_{1/4}^{(e)} B_{1/4}^{(f)} B_{1/2}^{(j)} B_{1/2}^{(j)}$ $X_{1/4}^{(i)} X_{1/4}^{(i)} X_{1/4}^{(i)} X_{1/4}^{(i)} X_{1/2}^{(j)} X_{1/2}^{(j)} X_{1/2}^{(j)} X_{1/2}^{(j)} X_{1/2}^{(j)} X_{1/2}^{(j)}$
12	$(0, 0, \theta, \theta, 0, 0, 0, 0, \theta, \theta, 0, 0)^1$	$C2/c$ (No. 15)	4	$\mathbf{a}_1 + \mathbf{a}_2 - \mathbf{a}_3, 2\mathbf{a}_2, \mathbf{a}_1 + \mathbf{a}_3$	$A_{1/2}^{(f)} A_{1/2}^{(f)} B_{1/4}^{(d)} B_{1/4}^{(e)} B_{1/4}^{(e)} B_{1/2}^{(f)} B_{1/2}^{(f)}$ $X_{1/2}^{(f)} X_{1/2}^{(f)} X_{1/2}^{(f)} X_{1/2}^{(f)} X_{1/2}^{(f)} X_{1/2}^{(f)} X_{1/2}^{(f)} X_{1/2}^{(f)}$
13	$(0, 0, \theta, \theta, 0, 0, 0, 0, 0, 0, 0)^1$ $(\xi)^4_{sec}$	$I\bar{4}2d$ (No. 122)	4	$\mathbf{a}_1 + \mathbf{a}_2 - \mathbf{a}_3, 2\mathbf{a}_2, \mathbf{a}_1 + \mathbf{a}_3$	$A_{1/4}^{(a)} A_{1/4}^{(b)} A_{1/2}^{(d)} B^{(e)} B^{(e)} X^{(e)} X^{(e)} X^{(e)} X^{(e)}$
14	$(0, 0, \theta, 0, 0, 0, 0, 0, 0, \theta, 0, 0)^1$ $(0, 0, \varphi, \varphi, 0, 0)^3_{sec}$	$C2/m$ (No. 12)	4	$\mathbf{a}_1 + \mathbf{a}_2 - \mathbf{a}_3, 2\mathbf{a}_2, \mathbf{a}_1 + \mathbf{a}_3$	$A_{1/4}^{(i)} A_{1/4}^{(i)} A_{1/2}^{(j)} B_{1/8}^{(c)} B_{1/8}^{(d)} B_{1/4}^{(e)} B_{1/4}^{(f)} B_{1/2}^{(j)} B_{1/2}^{(j)} X_{1/4}^{(i)} X_{1/4}^{(i)}$ $X_{1/4}^{(i)} X_{1/4}^{(i)} X_{1/2}^{(j)} X_{1/2}^{(j)} X_{1/2}^{(j)} X_{1/2}^{(j)} X_{1/2}^{(j)} X_{1/2}^{(j)}$

For finding all possible low-symmetry phases and corresponding order parameters c_i , the basic functions φ_i of irreps of a group of structure symmetry of the high-symmetry phase, and also the stratification of Wyckoff positions, we used the group-theoretical method which was described in detail in Gufan (1971, 1982), Chechin (1989), Sahnenko *et al.* (1986) and Vinberg *et al.* (1974). We checked also the separate results obtained by our method by means of the *ISOTROPY* program (Stokes & Hatch, 2007; Stokes *et al.*, 2002).

Calculation of possible ordered crystal phases by group-theoretical methods of the phase transition theory may be made in the following way. In the first step, when limiting by maximum possible primitive cell multiplication, a permutation representation of the given crystal is built. This permutation representation of the symmetry group of the initial high-symmetry phase can be built using probabilities of filling the Wyckoff positions by atoms. The dimension of this representation equals the position number in the extended cell. The extended cell, in its turn, is defined by minimum translations α_j . The translations of the extended cell (\mathbf{a}_j) are defined from $\exp(ik_L \mathbf{a}_j) = 1$, where k_L are vectors of all beams L of stars $\{k\}$, entering into the channel of the phase transition. We can carry out the research in two ways.

The first way consists of expanding the permutation representation into irreps. For each irrep of the symmetry group of the initial phase symmetry, all possible phases based on the Landau one critical representation are found.

In the second way the permutation representation is considered. All possible phases are found by group-theoretical methods. The permutation representation is not expanded on the irreps. This method is very cumbersome, but the solution of the task will be complete. This approach is used in our work.

The permutation representation has, as a rule, a large dimension and generates a very great number of low-symmetry phases. In this work we give the results concerning only binary and ternary atom ordering for each Wyckoff position of the spinel structure.

The spinel structure has a face-centred cubic lattice. For this lattice, the first Brillouin zone represents a body-centred lattice and contains four points of high symmetry, namely: $\mathbf{k}_{11}(\Gamma)$, $\mathbf{k}_{10}(X)$, $\mathbf{k}_{19}(L)$ and $\mathbf{k}_8(W)$ (Kovalev, 1993). To these points there are stars of the following wavevectors:

$$\mathbf{k}_{11} = 0, \mathbf{k}_{10} = 1/2(\mathbf{b}_1 + \mathbf{b}_2), \mathbf{k}_9 = 1/2(\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3),$$

$$\mathbf{k}_8 = \mathbf{b}_1/4 - \mathbf{b}_2/4 + \mathbf{b}_3/2.$$

Table 2
Binary and ternary cation ordering in Wyckoff position 16d of the spinel structure.

No.	Order parameters	Symbol of space group	V'/V	Translations of primitive cell of spinel structure	Structural formula
1	$(\xi, -\xi, \xi)^7$	$R\bar{3}2/m$ (No. 166)	1	a_1, a_2, a_3	$A^{(c)}B_{1/2}^{(b)}B_{3/2}^{(e)}X^{(c)}X_3^{(h)}$
2	$(\varphi, 0, \varphi, 0, \varphi, 0)^3$	$P\bar{4}3m$ (No. 215)	4	$a_1+a_2+a_3, 2a_2, 2a_3$	$A_{1/8}^{(a)}A_{3/8}^{(c)}A_{1/2}^{(e)}B_{1/2}^{(e)}B_{3/2}^{(e)}X_{1/2}^{(e)}X_{1/2}^{(e)}X_{3/2}^{(f)}X_{3/2}^{(f)}$
3	$(0, \xi, 0)^7$	$Imma$ (No. 74)	1	a_1, a_2, a_3	$A^{(e)}B^{(b)}B^{(d)}X_2^{(h)}X_2^{(i)}$
4	$(0, \varphi, 0, \varphi, 0, -\varphi)^1$	$P4_332$ (No. 212) $P4_132$ (No. 213)	4	$a_1+a_2+a_3, 2a_2, 2a_1$	$A^{(c)}B_{1/2}^{(a)}B_{3/2}^{(d)}X^{(c)}X_3^{(e)}$
5	$(0, \varphi, 0, 0, 0, 0)^3$	$P\bar{4}m2$ (No. 115)	2	$a_1+a_3, a_2, 2a_1$	$A_{1/4}^{(a)}A_{1/4}^{(c)}A_{1/2}^{(e)}B^{(j)}B^{(k)}X^{(j)}X^{(j)}X^{(k)}X^{(k)}$
6	$(0, 0, 0, 0, 0, \varphi)^1$	$P4_122$ (No. 91) $P4_322$ (No. 95)	2	$a_2+a_3, 2a_2, a_1$	$A^{(c)}B^{(a)}B^{(b)}X_2^{(d)}X_2^{(d)}$
7	$(0, \varphi, 0, 0, \varphi, 0)^1$ $(0, 0, 0, \varphi, 0, 0)^3_{sec}$	$P\bar{4}2_1m$ (No. 113)	4	$a_1+a_2+a_3, 2a_2, 2a_1$	$A_{1/4}^{(b)}A_{1/4}^{(c)}A_{1/2}^{(e)}B_{1/2}^{(e)}B_{1/2}^{(e)}B^{(f)}X_{1/2}^{(e)}X_{1/2}^{(e)}X_{1/2}^{(e)}X_{1/2}^{(f)}X_{1/2}^{(f)}$
8	$(0, 0, \varphi, \varphi, 0, 0)^1$ $(0, \xi, 0)^7_{sec}$	$Pbmn$ (No. 53)	2	$a_1+a_3, a_2, 2a_1$	$A^{(h)}B_{1/2}^{(b)}B_{1/2}^{(e)}B^{(g)}X^{(h)}X^{(i)}X_2^{(i)}$
9	$(0, 0, \eta, 0)^4$ $(\xi, -\xi, \xi)^7_{sec}$	$R\bar{3}2/m$ (No. 166)	2	$a_1, a_3, 2a_2$	$A_{1/2}^{(c)}A_{1/2}^{(e)}B_{1/4}^{(a)}B_{3/2}^{(h)}X_{1/2}^{(c)}X_{1/2}^{(e)}X_{3/2}^{(h)}X_{3/2}^{(h)}$
10	$(0, 0, \eta, 0)^1$ $(\xi, -\xi, \xi)^7_{sec}$	$R\bar{3}2/m$ (No. 166)	2	$a_1, a_3, 2a_2$	$A_{1/2}^{(c)}A_{1/2}^{(e)}B_{1/2}^{(c)}B_{3/4}^{(d)}B_{3/4}^{(e)}X_{1/2}^{(c)}X_{1/2}^{(e)}X_{3/2}^{(h)}X_{3/2}^{(h)}$
11	$(\varphi, 0, 0, 0, 0, -\varphi)^3$ $(0, 0, \varphi, 0, 0, 0)^1_{sec}$	$P4_122$ (No. 91) $P4_322$ (No. 95)	4	$a_1+a_2+a_3, 2a_2, 2a_3$	$A_{1/2}^{(a)}A_{1/2}^{(b)}B_{1/2}^{(c)}B^{(d)}X^{(d)}X^{(d)}X^{(d)}X^{(d)}$
12	$(0, \varphi_1, 0, \varphi_2, 0, -\varphi_1)^1$	$P4_12_12$ (No. 92) $P4_32_12$ (No. 96)	4	$a_1+a_2+a_3, 2a_2, 2a_1$	$A^{(b)}B_{1/2}^{(a)}B_{1/2}^{(a)}B^{(b)}X^{(b)}X^{(b)}X^{(b)}X^{(b)}$
13	$(\xi_1, -\xi_1, \xi_2)^7$	$C2/m$ (No. 12)	1	a_1, a_2, a_3	$A^{(i)}B_{1/2}^{(b)}B_{1/2}^{(d)}B^{(e)}X^{(i)}X^{(i)}X_2^{(f)}$
14	$(\varphi, \varphi, 0, 0, 0, 0)^3$ $(0, 0, \xi)^7_{sec}$	$Pcmm$ (No. 51)	2	$a_1+a_2, a_3, 2a_1$	$A_{1/2}^{(e)}A_{1/2}^{(f)}B_{1/2}^{(b)}B_{1/2}^{(c)}B^{(k)}X^{(k)}X^{(k)}X^{(k)}X^{(k)}$
15	$(\varphi_1, 0, \varphi_2, 0, -\varphi_2, 0)^3$	$P\bar{4}2m$ (No. 111)	4	$a_1+a_2+a_3, 2a_2, 2a_1$	$A_{1/8}^{(a)}A_{1/8}^{(f)}A_{1/4}^{(m)}A_{1/2}^{(n)}B_{1/2}^{(n)}B^{(o)}X_{1/2}^{(n)}X_{1/2}^{(n)}X_{1/2}^{(n)}X_{1/2}^{(n)}X^{(o)}X^{(o)}$
16	$(0, 0, \theta, \theta, 0, 0, 0, 0, 0, 0, 0)^1$	$I\bar{4}2d$ (No. 122)	4	$a_1+a_2-a_3, 2a_2, a_1+a_3$	$A_{1/4}^{(a)}A_{1/4}^{(d)}A_{1/2}^{(e)}B^{(e)}X^{(e)}X^{(e)}X^{(e)}X^{(e)}$
17	$(0, 0, 0, 0, 0, 0, \theta, 0, 0, 0, 0, 0)^1$ $(\varphi, 0, 0, 0, 0, 0)^3_{sec}$	$I\bar{4}2m$ (No. 121)	4	$a_1+a_2-a_3, 2a_2, a_1+a_3$	$A_{1/8}^{(a)}A_{1/8}^{(d)}A_{1/4}^{(i)}A_{1/2}^{(j)}B_{1/2}^{(j)}B^{(i)}X_{1/2}^{(i)}X_{1/2}^{(i)}X_{1/2}^{(i)}X_{1/2}^{(i)}X^{(i)}X^{(i)}$
18	$(0, \theta, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0)^2$ $(0, \varphi, 0, 0, 0, 0)^3_{sec}$	$I\bar{4}2m$ (No. 121)	4	$a_1+a_2-a_3, 2a_2, a_1+a_3$	$A_{1/4}^{(a)}A_{1/4}^{(i)}A_{1/2}^{(j)}B_{1/2}^{(j)}B^{(i)}X_{1/2}^{(i)}X_{1/2}^{(i)}X_{1/2}^{(i)}X_{1/2}^{(i)}X^{(i)}X^{(i)}$
19	$(0, 0, \theta, \theta, 0, 0, 0, 0, 0, 0, 0, 0)^2$	$I\bar{4}2d$ (No. 122)	4	$a_1+a_2-a_3, 2a_2, a_1+a_3$	$A_{1/2}^{(d)}A_{1/2}^{(e)}B^{(e)}B^{(e)}X^{(e)}X^{(e)}X^{(e)}X^{(e)}$

The indexing of vectors and irreps is given accordingly (Kovalev, 1993). There are ten irreps of the wavevector κ_{11} (four one-dimensional, two two-dimensional and four three-dimensional); four six-dimensional irreps of the wavevector κ_{10} , four four- and two eight-dimensional irreps of the wavevector κ_9 , and two 12-dimensional irreps of the wavevector κ_8 . Thus all-in-all there are 22 irreps.

All irreps of the wavevector κ_8 and also two irreps of the wavevector κ_{10} (τ_{10-3} and τ_{10-4}) do not satisfy the Lifshitz criterion, *i.e.* they induce incommensurate phases. Nevertheless, we included these irreps in our analysis, as among the low-symmetry phases induced by these representations there are also commensurate phases. In the full permutation representation only irreps relating to the wavevectors $\mathbf{k}_{11}(\Gamma)$, $\mathbf{k}_{10}(X)$, $\mathbf{k}_9(L)$ and $\mathbf{k}_8(W)$ are included. When calculating the number of binary and ternary phases only those phases were

taken into account that were generated by irreps concerning the above-mentioned wavevectors.

3. Types of cation order in tetrahedral spinel positions

The permutation representation on Wyckoff position 8a of the space group $Fd\bar{3}m$ generates 305 low-symmetry phases. The composition of the permutation representation is as follows:¹

$$\mathbf{k}_8(\tau_1) + \mathbf{k}_9(\tau_1 + \tau_4) + \mathbf{k}_{10}(\tau_3) + \mathbf{k}_{11}(\tau_4(A_{2u})). \quad (1)$$

The representation $\mathbf{k}_{11}(\tau_1(A_{1g}))$ always enters into the permutation representations. We do not give it in equation (1) and in the other equations because it does not lead to a symmetry change and a new type of atom ordering. We do not give the multiplicity of irreps entering into permutation representations on the Wyckoff positions of the space group $Fd\bar{3}m$ because they are unnecessary for defining possible types of ordered phases.

In Table 1 we give the binary and ternary ordered phases. The total number of these phases is 14. In the same table stratification of Wyckoff position 8a of the space group $Fd\bar{3}m$ is presented. As seen from Table 1, among these phases there are seven binary (phases 1–6, 12) and seven ternary (phases 7–11, 14) superstructures (Table 1). The types of binary super-

¹ The correspondence of designations by Kovalev (1993) 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 $k_{11}(\Gamma)$: $k_{11}\tau_1(A_{1g}) - GM1+$, $k_{11}\tau_2(A_{1u}) - GM1-$, $k_{11}\tau_3(A_{2g}) - GM2+$, $k_{11}\tau_4(A_{2u}) - GM2-$, $k_{11}\tau_5(E_g) - GM3+$, $k_{11}\tau_6(E_u) - GM3-$, $k_{11}\tau_7(F_{2g}) - GM5+$, $k_{11}\tau_8(F_{2u}) - GM5-$, $k_{11}\tau_9(F_{1g}) - GM4+$, $k_{11}\tau_{10}(F_{1u}) - GM4-$.

Table 3
Binary and ternary cation ordering in Wyckoff position 32*e* of the spinel structure.

No.	Order parameters	Symbol of space group	V'/V	Translations of primitive cell of spinel structure	Structural formula
1	$(0, \xi, 0)^{10}$	$I4_1md$ (No. 109)	1	$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$	$A^{(a)}B_2^{(b)}X_2^{(b)}X_2^{(b)}$
2	$(\xi)^4$	$F\bar{4}3m$ (No. 216)	1	$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$	$A^{(a)}A^{(d)}B_4^{(e)}X_4^{(e)}X_4^{(e)}$
3	$(\xi, -\xi, \xi)^7$	$R\bar{3}2/m$ (No. 166)	1	$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$	$A^{(c)}B_{1/2}^{(b)}B_{3/2}^{(e)}X^{(c)}X_3^{(h)}$
4	$(0, \varphi, 0, \varphi, 0, -\varphi)^1$	$P4_332$ (No. 212) $P4_132$ (No. 213)	4	$\mathbf{a}_1+\mathbf{a}_2+\mathbf{a}_3, 2\mathbf{a}_2, 2\mathbf{a}_1$	$A^{(c)}B_{1/2}^{(a)}B_{3/2}^{(d)}X^{(c)}X_3^{(e)}$
5	$(0, 0, \varphi, 0, 0, 0)^2$	$P4_12_12$ (No. 92) $P4_32_12$ (No. 96)	2	$\mathbf{a}_1+\mathbf{a}_3, \mathbf{a}_2, 2\mathbf{a}_1$	$A^{(a)}B_2^{(b)}X_2^{(b)}X_2^{(b)}$
6	$(0, 0, \xi)^7$	$Imma$ (No. 74)	1	$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$	$A^{(e)}B^{(b)}B^{(d)}X_2^{(h)}X_2^{(i)}$
7	$(0, \varphi, 0, 0, 0, 0)^1$	$P4_122$ (No. 91) $P4_322$ (No. 95)	2	$\mathbf{a}_1+\mathbf{a}_2, 2\mathbf{a}_1, \mathbf{a}_3$	$A^{(c)}B^{(a)}B^{(b)}X_2^{(d)}X_2^{(d)}$
8	$(\xi, -\xi, 0)^{10} (0, 0, \xi)^7 sec$	$Ima2$ (No. 46)	1	$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$	$A^{(b)}B^{(a)}B^{(b)}X^{(b)}X^{(b)}X_2^{(c)}$
9	$(\varphi, -\varphi, 0, 0, 0, 0)^1 (0, 0, \xi)^7 sec$	$Pbmm$ (No. 53)	2	$\mathbf{a}_1+\mathbf{a}_2, \mathbf{a}_3, 2\mathbf{a}_1$	$A^{(h)}B_{1/2}^{(b)}B_{1/2}^{(c)}B^{(g)}X^{(h)}X^{(h)}X_2^{(i)}$
10	$(\varphi, \varphi, 0, 0, 0, 0)^2 (0, 0, \xi)^7 sec$	$Pbnm$ (No. 62)	2	$\mathbf{a}_1+\mathbf{a}_2, \mathbf{a}_3, 2\mathbf{a}_1$	$A^{(c)}B^{(c)}B^{(b)}X^{(c)}X^{(c)}X_2^{(d)}$
11	$(\xi_1, \xi_2, -\xi_1)^7$	$C2/m$ (No. 12)	1	$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$	$A^{(i)}B_{1/2}^{(b)}B_{1/2}^{(d)}B^{(e)}X^{(i)}X^{(i)}X_2^{(j)}$

structures that are possible are 1:1, 1:3, and the ternary ones are 1:1:2, 1:3:4. In Table 1 improper order parameters are also given. They are marked by 'sec'.

4. Types of cation order in octahedral spinel positions

Cation ordering in octahedral spinel positions has been investigated before (Billet *et al.*, 1967). Simple geometrical consideration of possible superstructures with 1:1 order type in an octahedral sublattice of a spinel led to 12 870 variants. The authors limited their analysis to structures with face-centred cells and as such 198 structures are possible. Limitations of a physical character were introduced. Finally, the authors came to the conclusion that two superstructures with 1:1 order existed in an octahedral spinel sublattice (Billet *et al.*, 1967). We obtained other results. Let us consider this problem in detail.

The permutation representation on Wyckoff position 16*d* of the space group $Fd\bar{3}m$ induces 537 low-symmetry phases. Among them there are 19 phases with binary and ternary atom ordering. The composition of the permutation representation is as follows:

$$\mathbf{k}_8(\tau_1 + \tau_2) + \mathbf{k}_9(\tau_1 + \tau_4 + \tau_5) + \mathbf{k}_{10}(\tau_1 + \tau_3) + \mathbf{k}_{11}(\tau_7(F_{2g})). \quad (2)$$

These phases and the stratifications of Wyckoff position 16*d* of the space group $Fd\bar{3}m$ are given in Table 2. Among these phases there are eight binary (phases 1–6) and 11 ternary (phases 7–15) superstructures (Table 2).

The following types of binary superstructures are possible: 1:1 and 1:3. Ternary superstructures of types 1:1:6, 2:3:3 and 1:1:2 are possible. Among these superstructures we have four pairs of enantiomorphic ordered spinel modifications.

When comparing equations (1) and (2) it can be stated that there are the same irreps. This means that, on atom ordering

on one Wyckoff position (8*a* or 16*d*) according to these irreps, forced atom ordering will take place on the other Wyckoff position.

5. Types of anion order in spinels

The permutation representation on Wyckoff position 32*e* of the space group $Fd\bar{3}m$ generates 595 low-symmetry ordered phases. The composition of the permutation representation is as follows:

$$\mathbf{k}_8(\tau_1 + \tau_2) + \mathbf{k}_9(\tau_1 + \tau_4 + \tau_5 + \tau_6) + \mathbf{k}_{10}(\tau_1 + \tau_3 + \tau_2) + \mathbf{k}_{11}(\tau_4(A_{2u}) + \tau_7(F_{2g}) + \tau_{10}(F_{1u})). \quad (3)$$

There are only 11 binary and ternary ordered phases. These phases and the stratifications of Wyckoff position 32*e* of the space group $Fd\bar{3}m$ are given in Table 3. As can be seen from Table 3, among these phases there are seven binary (phases 1–7) and four ternary (phases 8–11) superstructures. The appearance of each binary and ternary superstructure is connected with one irrep. Possible types of ordering are the following: types of binary superstructures are 1:1 and 1:3, the type of the ternary one is 1:1:2. From Table 3 it is seen that in some cases, on atomic ordering in Wyckoff position 32*e* of the space group $Fd\bar{3}m$ the forced stratification of Wyckoff positions 8*a* and 16*d* takes place.

It should be emphasized that among binary superstructures there are three pairs of enantiomorphic modifications of ordered spinels. Irreps of wavevector \mathbf{k}_8 do not generate binary and ternary superstructures.

6. Atom ordering in two sublattices

The permutation representation on Wyckoff positions 8*a* and 16*d* of the space group $Fd\bar{3}m$ gives rise to 549 low-symmetry

Table 4

Simultaneous binary and ternary ordering in Wyckoff positions $8a$ and $16d$ of the spinel structure.

No.	Order parameters	Symbol of space group	V'/V	Translations of primitive cell of spinel structure	Structural formula
1	$(0, \varphi, 0, \varphi, 0, -\varphi)^{3A,B} (\xi)^{4A} sec$	$P\bar{4}3m$ (No. 215)	4	$a_1+a_2+a_3, 2a_2, 2a_1$	$\frac{A_{1/8}^{(a)} A_{3/8}^{(c)} A_{1/2}^{(e)} B_{1/2}^{(e)} B_{3/2}^{(i)} X_{1/2}^{(e)} X_{1/2}^{(e)} X_{3/2}^{(i)} X_{3/2}^{(i)}$
2	$(0, 0, \eta, 0)^{4A} (\xi, -\xi, \xi)^{7B}$	$R\bar{3}2/m$ (No. 166)	2	$a_1, a_3, 2a_2$	$\frac{A_{1/2}^{(c)} A_{1/2}^{(c)} B_{1/4}^{(a)} B_{1/4}^{(b)} B_{3/2}^{(i)} X_{1/2}^{(c)} X_{1/2}^{(c)} X_{3/2}^{(h)} X_{3/2}^{(h)}$
3	$(0, 0, \eta, 0)^{1A,B} (\xi, -\xi, \xi)^{7B} sec$	$R\bar{3}2/m$ (No. 166)	2	$a_1, a_3, 2a_2$	$\frac{A_{1/2}^{(c)} A_{1/2}^{(c)} B_{1/2}^{(e)} B_{3/4}^{(a)} B_{3/4}^{(b)} X_{1/2}^{(c)} X_{1/2}^{(c)} X_{3/2}^{(h)} X_{3/2}^{(h)}$
4	$(0, \varphi, 0, 0, 0, 0)^{3A,B} (\xi)^{4A} sec$	$P\bar{4}m2$ (No. 115)	2	$a_1+a_2, a_3, 2a_1$	$\frac{A_{1/4}^{(a)} A_{1/4}^{(c)} A_{1/2}^{(e)} B_{1/2}^{(e)} X^{(i)} X^{(i)} X^{(k)} X^{(k)}$
5	$(\varphi, 0, 0, 0, 0, -\varphi)^{3A,B}$ $(0, 0, \varphi, 0, 0, 0)^{1B} sec$	$P4_{32}$ (No. 91) $P4_322$ (No. 95)	4	$a_1+a_2+a_3, 2a_2, 2a_3$	$\frac{A_{1/2}^{(a)} A_{1/2}^{(b)} B_{1/2}^{(c)} B_{1/2}^{(d)} X^{(d)} X^{(d)} X^{(d)} X^{(d)}$
6	$(\varphi, \varphi, 0, 0, 0, 0)^{3A,B}$ $(0, 0, \xi)^{7B} sec$	$Pcmm$ (No. 51)	2	$a_2+a_3, a_1, 2a_2$	$\frac{A_{1/2}^{(e)} A_{1/2}^{(f)} B_{1/2}^{(b)} B_{1/2}^{(c)} B^{(k)} X^{(k)} X^{(k)} X^{(k)} X^{(k)}$
7	$(0, \varphi, 0, 0, \varphi, 0)^{1B} (\xi)^{4A}$ $(0, 0, 0, \varphi, 0, 0)^{3A,B} sec$	$P\bar{4}2_1m$ (No. 113)	4	$a_1+a_2+a_3, 2a_2, 2a_1$	$\frac{A_{1/4}^{(b)} A_{1/4}^{(c)} A_{1/2}^{(e)} B_{1/2}^{(e)} B_{1/2}^{(f)} B^{(f)} X_{1/2}^{(e)} X_{1/2}^{(e)} X_{1/2}^{(e)} X_{1/2}^{(e)} X^{(f)} X^{(f)}$
8	$(\xi)^{4A} (\xi, -\xi, \xi)^{7B}$	$R3m$ (No. 160)	1	a_1, a_2, a_3	$\frac{A_{1/2}^{(a)} A_{1/2}^{(a)} B_{1/2}^{(b)} B_{3/2}^{(i)} X_{1/2}^{(a)} X_{1/2}^{(a)} X_{3/2}^{(b)} X_{3/2}^{(b)}$
9	$(\xi)^{4A} (0, \xi, 0)^{7B}$	$Imm2$ (No. 44)	1	a_1, a_2, a_3	$\frac{A_{1/2}^{(a)} A_{1/2}^{(b)} B^{(d)} B^{(c)} X^{(d)} X^{(d)} X^{(c)} X^{(c)}$
10	$(\xi)^{4A} (0, \varphi, 0, \varphi, 0, -\varphi)^{1B}$	$P2_13$ (No. 198)	4	$a_1+a_2+a_3, 2a_2, 2a_1$	$\frac{A_{1/2}^{(a)} A_{1/2}^{(a)} B_{1/2}^{(b)} B_{3/2}^{(i)} X_{1/2}^{(a)} X_{1/2}^{(a)} X_{3/2}^{(b)} X_{3/2}^{(b)}$
11	$(\xi)^{4A} (0, 0, 0, 0, 0, \varphi)^{1B}$	$C222_1$ (No. 20)	2	$a_2+a_3, 2a_2, a_1$	$\frac{A_{1/2}^{(a)} A_{1/2}^{(b)} B^{(c)} B^{(c)} X^{(c)} X^{(c)} X^{(c)} X^{(c)}$
12	$(\xi)^{4A} (0, 0, \varphi, \varphi, 0, 0)^{1B}$ $(0, \xi, 0)^{7B} sec$	$Pmn2_1$ (No. 31)	2	$a_1+a_3, a_2, 2a_1$	$\frac{A_{1/2}^{(a)} A_{1/2}^{(a)} B_{1/2}^{(b)} B_{1/2}^{(b)} B^{(b)} X_{1/2}^{(a)} X_{1/2}^{(a)} X_{1/2}^{(a)} X_{1/2}^{(a)} X^{(b)} X^{(b)}$
13	$(\xi)^{4A} (\xi_1, -\xi_1, \xi_2)^{7B}$	Cm (No. 8)	1	a_1, a_2, a_3	$\frac{A_{1/2}^{(a)} A_{1/2}^{(a)} B_{1/2}^{(b)} B_{1/2}^{(b)} X_{1/2}^{(a)} X_{1/2}^{(a)} X_{1/2}^{(a)} X_{1/2}^{(a)} X^{(b)} X^{(b)}$
14	$(0, 0, \theta, \theta, 0, 0, 0, 0, 0, 0, 0, 0)^{1A,B}$ $(\xi)^{4A} sec$	$I\bar{4}2d$ (No. 122)	4	$a_1+a_2-a_3, 2a_2, a_1+a_3$	$\frac{A_{1/4}^{(a)} A_{1/4}^{(b)} A_{1/2}^{(e)} B^{(e)} B^{(e)} X^{(e)} X^{(e)} X^{(e)} X^{(e)}$
15	$(0, \theta, 0, 0, 0, 0, 0, 0, 0, 0, 0)^{2B}$ $(\xi)^{4A} (0, \varphi, 0, 0, 0, 0)^{3A,B} sec$	$I\bar{4}2m$ (No. 121)	4	$a_1+a_2-a_3, 2a_2, a_1+a_3$	$\frac{A_{1/4}^{(c)} A_{1/4}^{(e)} A_{1/2}^{(i)} B_{1/2}^{(i)} B_{1/2}^{(j)} B^j X_{1/2}^{(i)} X_{1/2}^{(i)} X_{1/2}^{(i)} X_{1/2}^{(i)} X^{(i)} X^{(i)}$
16	$(0, 0, \theta, \theta, 0, 0, 0, 0, 0, 0, 0)^{2B}$ $(\xi)^{4A}$	$I\bar{4}2d$ (No. 122)	4	$a_1+a_2-a_3, 2a_2, a_1+a_3$	$\frac{A_{1/2}^{(d)} A_{1/2}^{(c)} B^{(e)} B^{(e)} X^{(e)} X^{(e)} X^{(e)} X^{(e)}$

phases. The composition of the permutation representation is as follows:

$$\mathbf{k}_8(\tau_1 + \tau_2) + \mathbf{k}_9(\tau_1 + \tau_4 + \tau_5) + \mathbf{k}_{10}(\tau_1 + \tau_3) + \mathbf{k}_{11}(\tau_4(A_{2u}) + \tau_7(F_{2g})). \tag{4}$$

There are only 16 types of ordered phases if we consider only binary and ternary atomic ordering in each Wyckoff position. These phases and the stratifications of Wyckoff positions $8a$ and $16d$ of the space group $Fd\bar{3}m$ are given in Table 4. As seen from Table 4, among these phases there are five phases with binary order in tetrahedral and octahedral spinel sublattices of two types: $(1:1)^{8a}[1:3]^{16d}$, $(1:1)^{8a}[1:1]^{16d}$; six phases with binary and ternary orders of three types: $(1:1)^{8a}[1:1:6]^{16d}$, $(1:1)^{8a}[2:3:3]^{16d}$, $(1:1)^{8a}[1:1:2]^{16d}$; three phases with ternary and binary orders of two types: $(1:3:4)^{8a}[1:3]^{16d}$, $(1:1:2)^{8a}[1:1]^{16d}$; and two phases with ternary order in both spinel sublattices of two types: $(1:1:2)^{8a}[2:2:1]^{16d}$, $(1:1:2)^{8a}[1:1:2]^{16d}$.

7. Discussion

7.1. Cation order in tetrahedral positions of the spinel structure

The most widespread types of cation ordering in positions $8a$ are realized in structures with space groups $F\bar{4}3m$ [order parameter (ξ) , $\mathbf{k}_{11}(\tau_4(A_{2u}))$] and $R\bar{3}2/m$ [order parameter $(\eta, 0, 0, 0)$, $\mathbf{k}_9(\tau_4)$].

Ordered spinel structure with space group $F\bar{4}3m$. Phases with this symmetry are formed as a result of a phase transition of the second order from cubic spinel. For many spinels ($MgAl_2O_4$, $LiGaCr_4O_8$, $CdIn_2S_4$ etc.) a phase transition is really found experimentally (Suzuki & Kumazawa, 1980; Yamanaka & Takeuchi, 1983; Joubert & Durif, 1966). But there are also compounds, for example $LiXY_4O_8$ ($X = Ga, Fe, In; Y = Cr, Rh$), that exist in the ordered modification up to the temperature of melting (Joubert & Durif, 1966).

Irrep $\mathbf{k}_{11}(\tau_4(A_{2u}))$ enters into the permutation representation of a spinel on positions $8a$ and $32e$, and enters into the mechanical representation of a spinel on positions $16d$ and $32e$ (Gufan, 1971; Talanov, 1986b). The formation of a $F\bar{4}3m$ phase is accompanied by ordering of tetrahedral cations (1:1 order type) and anions (1:1 order type), and also by displacements of octahedral cations and anions. It was stated by calculation that the general structural formula of the ordered spinel is $A^{4a}A^{4c}B_4^{16e}X_4^{16e}X_4^{16e}$ (Talanov, 1986b). Features of the $F\bar{4}3m$ -phase structure are discussed in Talanov (1986b, 1996, 2004, 2005) and Talanov *et al.* (2008). In Fig. 1, the calculated structure of the ordered $F\bar{4}3m$ phase is shown. Metal clusters are the most interesting feature of this structure. Two neighbouring groups of octahedral cations and anions form the expanded and compressed tetrahedra (Fig. 2). The compressed tetrahedron of B cations can be considered as a metal cluster. Compressed tetrahedra have the linear size $(2^{1/2}/4)a$ and are located at a distance $(6^{1/2}/4)a$, where a is the parameter of a cubic elementary cell of a spinel structure.

Many ordered spinels have a similar structure, for example λ - $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$ (Julien *et al.*, 2006), $\text{Li}_{0.5}\text{Cr}_x\text{Ga}_{2.5-x}\text{O}_4$ ($x = 1.75$) (Arsen *et al.*, 1979; Arsen & Lenglet, 1980; Szymczak *et al.*, 1975), $\text{Li}_{0.5}\text{Fe}_{0.5}[\text{Cr}_2]\text{O}_4$ (Gorter, 1954), $\text{LiGaCr}_4\text{O}_8$ (Yamanaka & Takeuchi, 1983), $\text{GaV}_{4-x}\text{Mo}_x\text{S}_8$ ($0 \leq x \leq 4$) (Powell *et al.*, 2007), $\text{Cu}_{0.5}\text{In}_{0.5}\text{Cr}_2\text{S}_4$ (Sadykov *et al.*, 2001; Plumier, Sougi & Lecomte, 1977), $\text{Cu}_{0.5}\text{Fe}_{0.5}\text{Cr}_2\text{S}_4$ (Sadykov *et al.*, 2001), $\text{Ag}_{0.5}\text{In}_{0.5}\text{Cr}_2\text{S}_4$ (Plumier, Lecomte *et al.*, 1977), LiXY_4O_8 ($X = \text{Ga, Fe, In; Y} = \text{Cr, Rh}$) (Joubert & Durif, 1966), CdIn_2S_4 (Joubert & Durif, 1966; Cravetskiy *et al.*, 1992), MgAl_2O_4 (Suzuki & Kumazawa, 1980), $\text{Li}_{0.5}\text{Fe}_{1.0}\text{Rh}_{1.5}\text{O}_4$ (Kang & Kim, 2006), FeIn_2S_4 (Hill *et al.*, 1978) and others.

Ordered spinel structure with space group $R\bar{3}2/m$. This structure is formed as a result of ordering and displacements of tetrahedral and octahedral cations and anions in the spinel structure. The tetrahedral cations are ordered by the 1:1 type, the octahedral cations by the 1:1:6 type and the anions by the 1:1:3:3 type. The general structural formula of the ordered spinel should be $A_{1/2}^{2c}A_{1/2}^{2c}B_{1/4}^{1a}B_{1/4}^{1b}B_{3/2}^{6h}X_{1/2}^{2c}X_{1/2}^{2c}X_{3/2}^{6h}X_{3/2}^{6h}$ (for the rhombohedral representation of the structure) or $A_{1/2}^{6c}A_{1/2}^{6c}B_{1/4}^{3a}B_{1/4}^{3b}B_{3/2}^{18h}X_{1/2}^{6c}X_{1/2}^{6c}X_{3/2}^{18h}X_{3/2}^{18h}$ (for the hexagonal representation of the structure). In Fig. 3 the calculated structure of the ordered $R\bar{3}2/m$ phase is shown. The unusual feature of this structure is ‘molecular heptamers’ (Matsuno *et al.*, 2001, 2003; Nishiguchi & Onoda, 2002; Horibe *et al.*, 2006). The molecular heptamers consist of B^{3b} and B^{18h} atoms (Fig. 3d). The total number of B atoms in a metal cluster (heptamer) equals seven. Substances such as AlV_2O_4 , $\text{AlV}_{2-x}\text{Cr}_x\text{O}_4$ and $\text{Al}_{1-x}\text{Mg}_x\text{V}_2\text{O}_4$ (Matsuno *et al.*, 2001, 2003; Nishiguchi & Onoda, 2002; Horibe *et al.*, 2006), CuTi_2S_4 (Soheilnia *et al.*, 2004) and $\text{CuZr}_{1.86}\text{S}_4$ (Dong *et al.*, 2010) have the $R\bar{3}2/m$ structure.

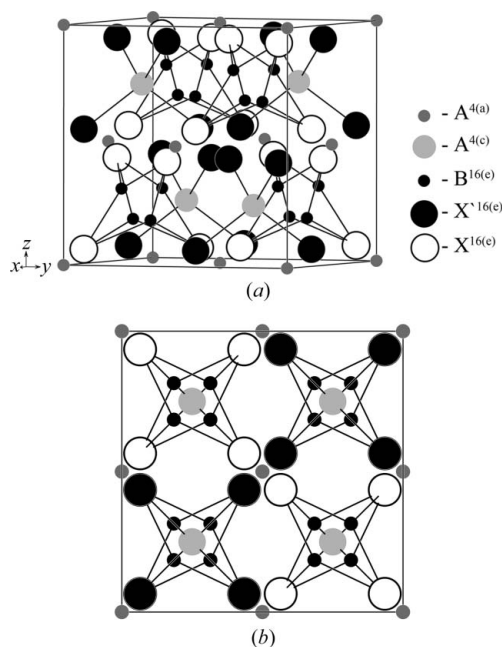


Figure 1
Calculated structure of an ordered spinel (space group $F\bar{4}3m$). Atomic presentation of the structure (a) and projection along (001) (b) of the ordered spinel structure.

7.2. Cation order in octahedral positions of the spinel structure

Among structures with cation order in the octahedral positions of a spinel, there are ones with space groups $P4_{1(3)}22$ [order parameter $(0, 0, 0, 0, 0, \varphi)$, $\mathbf{k}_{10}(\tau_1)$], $P4_{3(1)}32$ [order parameter $(0, \varphi, 0, \varphi, 0, -\varphi)$, $\mathbf{k}_{10}\tau_1$] and $Imma$ [order parameter $(0, \xi, 0)$, $\mathbf{k}_{11}(\tau_7)$].

The feature of structures of the ordered enantiomorphic $P4_122$ and $P4_322$ phases, and also the $P4_332$ and $P4_132$ phases, is that among the elements of symmetry of the space group of their structures there is no inversion and no symmetry planes, but only symmetry axes. Such crystals can exist in right- and left-hand forms, being mirror reflections of each other. By physical properties they are not distinguishable (except by optical activity). In LiFe_5O_8 enantiomorphic modifications exist as various domains in one sample (Van der Biest & Thomas, 1975).

Ordered spinel structure with enantiomorphic space groups $P4_122$ and $P4_322$. These structures are formed as a result of a phase transition with a critical parameter of order transformed by the six-dimensional irrep $\mathbf{k}_{10}(\tau_1)$. Octahedral cation ordering is of the 1:1 type. It is accompanied by displacements of tetrahedral and octahedral cations and also anions. In the low-symmetry phase the anions are ordered (the type of order is 1:1).

The structural formula of the low-symmetry phase should be $A^{4c}B^{4a}B^{4b}X_2^{8d}X_2^{8d}$. In Fig. 4 the structural features of the enantiomorphic phases are shown. The following substances crystallize in $P4_122$ and $P4_322$ structures: LiZnNbO_4 (Marin *et al.*, 1994), Li_2TeO_4 (Daniel *et al.*, 1977), A_2TiO_4 [where $A = \text{Zn}$

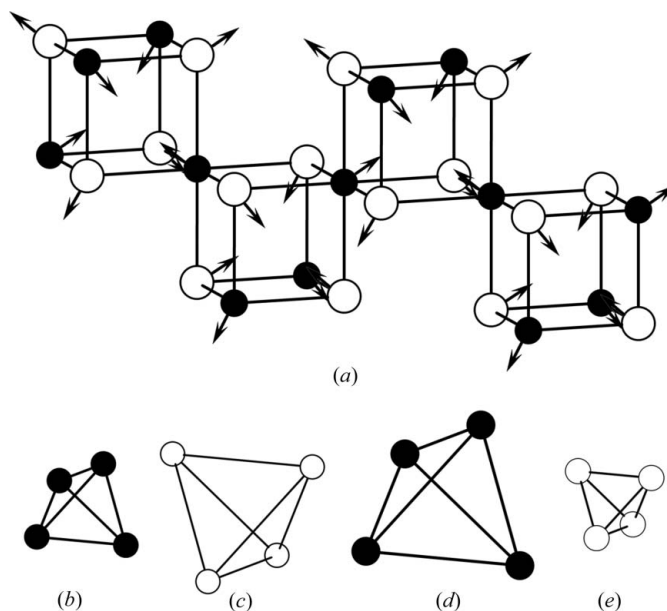


Figure 2
Structural mechanism of atomic cluster formation. Displacements of octahedral cations and anions in the adjacent octants of the spinel structure (a); compressed cluster B_4 (b), expanded cluster X_4 (c), expanded cluster B_4 (d) and compressed cluster X_4 (e).

(Marin *et al.*, 1994; Billiet & Poix, 1963; Billiet *et al.*, 1963; Vincent & Durif, 1966), Mn (Hardy *et al.*, 1964; Millard *et al.*, 1995) or Mg (Delanoye & Michel, 1969)], Zn_2GeO_4 (Millard *et al.*, 1995; Syono *et al.*, 1971), LiMnNbO_4 (Shukaev *et al.*, 2007) and $\text{Zn}_{0.8}\text{Co}_{1.2}\text{GeO}_4$ (Preudhomme & Tarte, 1980).

Ordered spinel structure with enantiomorphic space groups $P4_132$ and $P4_332$. As stated, these structures are also formed as a result of a phase transition with a critical parameter of order transformed by the six-dimensional irrep $\mathbf{k}_{10}(\tau_1)$. The critical irrep $\mathbf{k}_{10}\tau_1$ enters into the permutation representation of a

spinel on positions $16d$ and $32e$ and enters into the mechanical representation of a spinel on positions $8a$, $16d$ and $32e$. Therefore, lowering of crystal symmetry is caused by displacements of all types of atoms and ordering of octahedral cations and anions. In the low-symmetry phase, octahedral cations and anions are ordered by the 1:3 type in both cases. The structural formula of the ordered phase should be $A_2^{\text{sc}}B^{4b}B_3^{12d}X_2^{\text{sc}}X_6^{24e}$. Low-symmetry modifications of LiM_5O_8 ($M = \text{Al}, \text{Ga}$) (Ahman *et al.*, 1996; Datta & Roy, 1963; Tarte & Collongues, 1964), $\text{Zn}_3\text{Ni}_2\text{TeO}_8$ (Bayer, 1967), $\text{Zn}_2\text{Co}_3\text{TeO}_8$ (Bayer, 1967), $\text{CuMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (Blasse, 1966; Vandenberghe *et al.*, 1976), $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$ (Blasse, 1966; Vandenberghe *et al.*, 1976), $\text{Zn}_2\text{Mn}_3\text{O}_8$ (Joubert & Durif, 1964a), ZnMGe_3O_8 ($M = \text{Mn}, \text{Mg}$) (Joubert & Durif, 1964a), $\text{M}_2\text{Ge}_3\text{O}_8$ ($M = \text{Zn}, \text{Co}$) (Joubert & Durif, 1964a), ZnMTi_3O_8 ($M = \text{Mn}, \text{Cd}$) (Joubert & Durif, 1964a), $\text{M}_2\text{Ti}_3\text{O}_8$ ($M = \text{Zn}, \text{Mn}, \text{Co}$) (Joubert & Durif, 1964a), $\text{V}_2\text{Co}_3\text{O}_8$ (Joubert & Durif, 1964b), $\text{Li}_2\text{Mn}_3\text{CoO}_8$ (Joubert & Durif-Varambon, 1963), $\text{Li}_{0.5+0.5x}\text{Fe}_{2.5-1.5x}\text{Ti}_x\text{O}_4$ ($0 \leq x \leq 0.4$, $1.2 \leq x \leq 1.57$) (Arillo *et al.*, 2003), $\text{Na}_4\text{Ir}_3\text{O}_8$ (Okamoto *et al.*, 2007), LiMnTiO_4 (Arillo *et al.*, 2008), $\text{Na}_4\text{Sn}_3\text{O}_8$ (Iwasaki *et al.*, 2002), $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (Wang *et al.*, 2011), $\text{LiFe}_{5-x}\text{Mn}_x\text{O}_8$ ($0 \leq x \leq 1$) (Darul *et al.*, 2005), LiFe_5O_8 (Braun, 1952; Widatallah *et al.*, 2005), $\text{LiMg}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$ (Wagemaker *et al.*, 2004), $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (Kim *et al.*, 2004), $\text{Li}_{1.25}\text{Fe}_{0.25}\text{Ti}_{1.5}\text{O}_4$ (Reale *et al.*, 2003), $\text{Li}_2\text{Mn}_3\text{MO}_8$ ($M = \text{Mg}, \text{Zn}$) (Strobel *et al.*, 2003), $\text{LiMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{CuMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (Branford *et al.*, 2002), $\text{Li}_x\text{Mg}_{1-2x}\text{Fe}_{2+x}\text{O}_4$ ($x \geq 0.40$) (Antic *et al.*, 2002), $\text{LiMg}_x\text{Mn}_{2-x}\text{O}_4$ ($x > 1$) (Singh *et al.*, 2009), $\text{Li}_2\text{CoTi}_3\text{O}_8$ (Reeves *et al.*, 2007), $\text{Li}_2\text{Zn}_3\text{O}_8$, $\text{Li}_2\text{Ge}_3\text{O}_8$ (Hirota *et al.*, 1988), $\text{LiM}_{0.5}\text{Ti}_{1.5}\text{O}_4$, $\text{LiM}_{0.5}\text{Ge}_{1.5}\text{O}_4$ ($M = \text{Mg}, \text{Co}, \text{Ni}, \text{Zn}$) (Kawai *et al.*, 1998; Hernander *et al.*, 1996), $\text{Li}_{1.33x}\text{Co}_{2-2x}\text{Ti}_{1+0.67x}\text{O}_4$ (Kremenović & Antic, 2004), $\text{Li}_{1-0.5x}\text{Fe}_{2.5x}\text{Mn}_{2-2x}\text{O}_4$

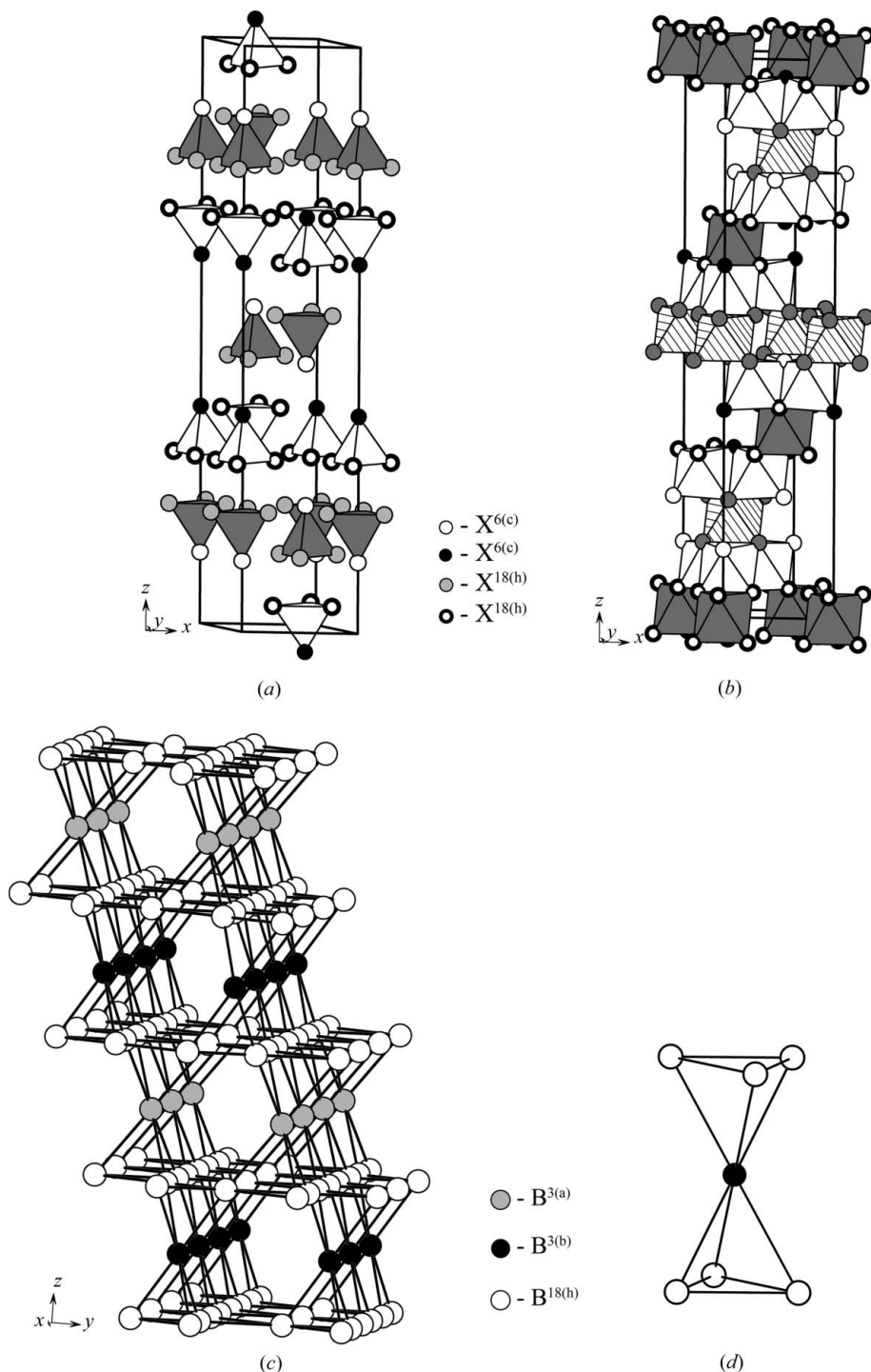


Figure 3 Fragments of the calculated ordered $R\bar{3}2/m$ structure. Presentation of the ordered spinel structure as two tetrahedra (white and grey), formed by two types of atoms A^{6c} and A^{6c} (a); presentation of the ordered spinel structure as three octahedra types (white, grey and dashed), formed by atoms B^{3a} , B^{3b} and B^{18h} (b); presentation of the ordered spinel structure as two types of 'molecules' – heptamers (c); and the 'molecule' – heptamer $B^{3b}[B^{18h}]_6$ (d).

(Kremenović & Antic, 2004), $\text{LiMn}_{2-y}\text{Ti}_y\text{O}_4$ ($y > 1$) (Petrov *et al.*, 2005), $\text{LiFe}_{0.5}\text{Ti}_{1.5}\text{O}_4$ (Avdeev *et al.*, 2007) and others have the structures of ordered $P4_132$ and $P4_332$ phases. The features of the calculated $P4_132$ and $P4_332$ structures are shown in Fig. 5.

Ordered spinel structure with space group $Imma$. This structure is generated by irrep $\mathbf{k}_{11}(\tau_7)$. This irrep enters into the mechanical representation of the spinel structure on positions $8a$ and $32e$ and enters into the permutation representation of a spinel on positions $16d$ and $32e$. Therefore, a low-symmetry modification of the $Imma$ phase is formed as a result of displacements of tetrahedral cations and anions and also ordering of octahedral cations and anions (in both cases the type of order is 1:1). A structural formula of the low-symmetry phase should be $A^{4e}B^{4a}B^{4d}X_2^{8h}X_2^{8i}$. The calculated structure is shown in Fig. 6. This structure contains chains of octahedra ($B^{4a}X_2^{8h}X_4^{8i}$ and $B^{4d}X_4^{8h}X_2^{8i}$) shared by edges, running along the y and x axes, respectively (Fig. 6c). The low-symmetry modifications of Li_2CoCl_4 (Wussow *et al.*, 1989), Li_2MnBr_4 (Kanno *et al.*, 1986), Li_2MgBr_4 (Smirnov, 1966), LiVCuO_4 (Joubert *et al.*, 1965), $\text{Li}_{1-x}\text{CuVO}_4$ ($0 \leq x \leq 0.2$) (Kanno *et al.*, 1992), LiSbZnO_4 (Keramidebs *et al.*, 1975) and Li_2FeCl_4 (Lutz *et al.*, 1989) have the $Imma$ structure.

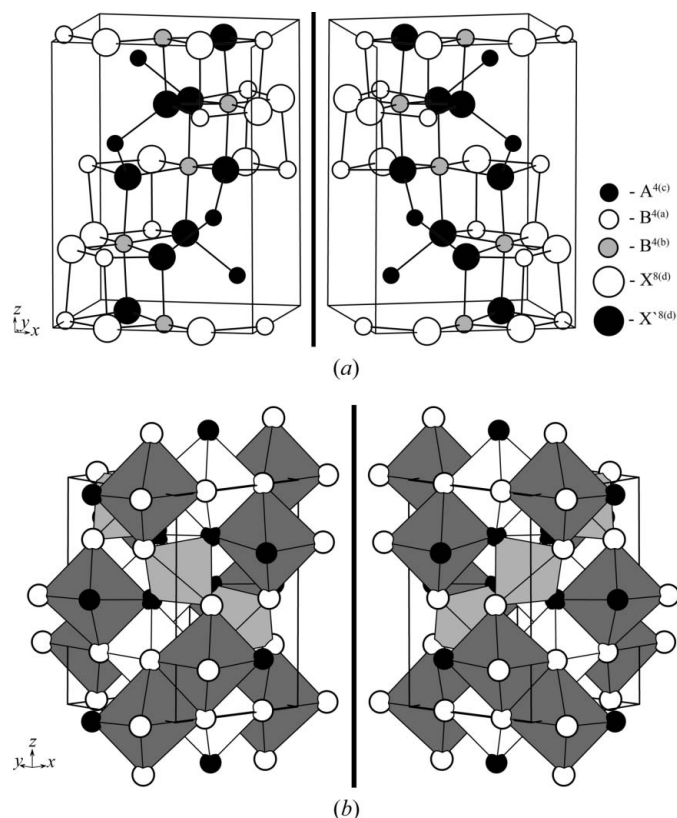


Figure 4
Calculated low-symmetry spinel structure with enantiomorphic space groups $P4_122$ and $P4_322$. Atom presentation of the ordered enantiomorphic spinel structures (atoms B^{4a} and B^{4b} are in the centres of white and dark octahedra) (a); polyhedral presentation of the ordered enantiomorphic spinel structures (b). The line between the structures indicates a mirror.

7.3. Anion order in the spinel structure

The typical examples of anion ordering in Wyckoff position $32e$ are spinel low-symmetry modifications with space groups $F\bar{4}3m$ [order parameter (ξ), $\mathbf{k}_{11}(\tau_4)$], $R\bar{3}2/m$ [order parameter (ξ , $-\xi$, ξ), $\mathbf{k}_{11}(\tau_7)$], and $P4_12_12$ and $P4_32_12$ [order parameter ($0, 0, \varphi, 0, 0, 0$), $\mathbf{k}_{10}(\tau_2)$].

Ordered spinel structure with space group $F\bar{4}3m$. We have already considered the structure of the $F\bar{4}3m$ phase. A special case of an ordered spinel structure is the structure of the Chevrel phases. The structure of these phases can be presented as a structure of defect spinels with ordering of tetrahedral cations and anions of the 1:1 type. If there are no A^{4a} and A^{4c} atoms at all, or only some of these atoms are absent, various types of Chevrel phases can be obtained (Talanov, 2005; Besnard *et al.*, 2003). For example, if there are no A^{4a} and A^{4c} atoms, then a formula $B_4^{16e}X_4^{16e}X_4^{16e}$ is obtained. This formula corresponds to the $\text{Re}_4\text{Te}_4\text{S}_4$ structure (Fedorov *et al.*, 1994, 1996). If only one type of atom A in the general formula is absent, then we have the formula $A^{4a}B_4^{16e}X_4^{16e}X_4^{16e}$. Such a formula describes the structures of GaMo_4O_8 (Besnard *et al.*, 2003) and $\text{Re}_4\text{As}_6\text{S}_3$ (Besnard *et al.*, 2003). If the positions of A^{4a} and A^{4c} atoms are partly occupied, then this

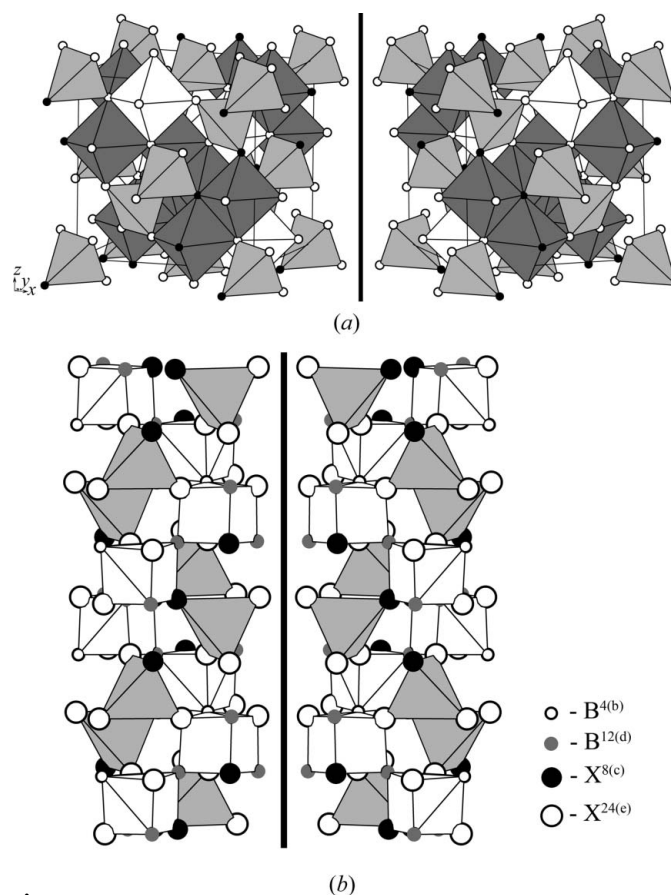


Figure 5
Calculated low-symmetry spinel structure with enantiomorphic space groups $P4_132$ and $P4_332$. Polyhedral presentation of the ordered enantiomorphic spinel structures (atoms B^{4b} and B^{12d} are in the centres of white and dark octahedra) (a); double spiral from tetrahedra and hexahedra (b). The line between the structures indicates a mirror.

formula describes the structures of such substances as $\text{Ga}_{1.33}\text{Cr}_4\text{S}_8$ (Besnard *et al.*, 2003) and $\text{Ga}_{0.5}\text{V}_2\text{S}_2\text{Se}_2$ (Haeu-seler *et al.*, 2001).

The structures of the Chevrel phases, their properties and features of the structures are genetically connected with the structure of ordered spinels. In particular, on cation ordering of the 1:1 type in tetrahedral positions of AB_2X_4 spinel, B_4 clusters from metal atoms and anions are formed (Talanov *et al.*, 2008) (Fig. 2). The structure of the Chevrel phases ‘inherits’ four types of clusters from the ordered spinel structure [this fact was established as a result of theoretical

research into the structural mechanism of ordered spinel formation with $F\bar{4}3m$ symmetry (Talanov *et al.*, 2008)].

We believe that the formation of these clusters causes the original physical properties of the Chevrel phases. In Figs. 7 and 8, examples of calculated structures of the Chevrel phases are given. In particular, Re_4 clusters exist in structures of the Chevrel phases such as $\text{Re}_4\text{As}_6\text{S}_3$ (Figs. 7*a–c*) and $\text{Re}_4\text{Te}_4\text{S}_4$ (Fig. 8).

Ordered spinel structure with space group $R\bar{3}2/m$. This structure is generated by irrep $\mathbf{k}_{11}(\tau_7)$. This irrep enters into the mechanical representation of the spinel structure on positions 8*a* and 32*e* and enters into the permutation representation of the spinel on positions 16*d* and 32*e*. This means that the low-symmetry phase formation is connected with displacements of tetrahedral cations and anions and also with ordering of octahedral cations and anions (in both cases the types of order are the same, *i.e.* 1:3). The structural formula of a low-symmetry phase should be $A^{2c}B_{1/2}^{1a}B_{3/2}^{3d}X^{2c}X_3^{6h}$. In Fig. 9,

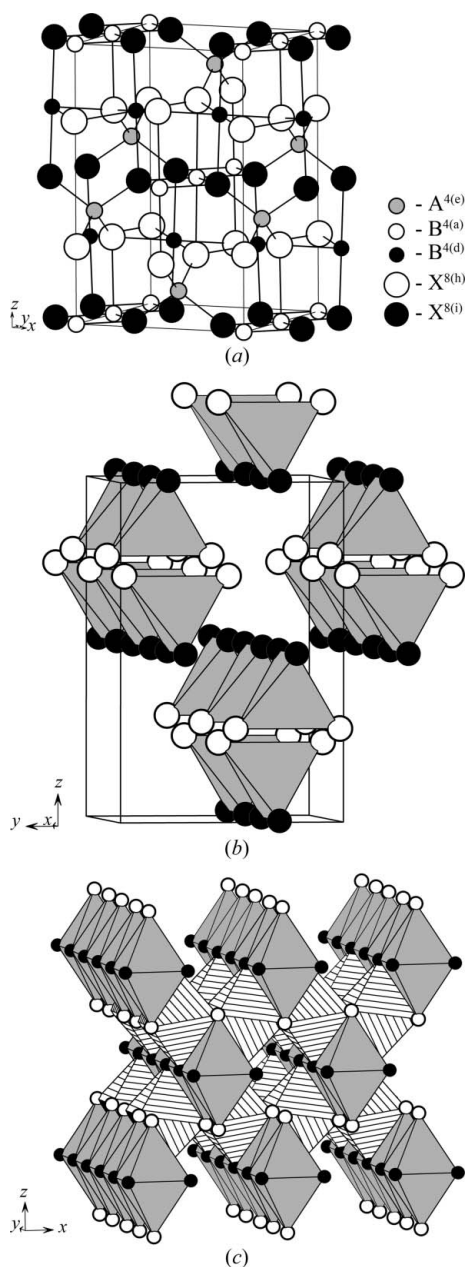


Figure 6
Calculated low-symmetry ordered spinel structure with space group $Imma$. Atom presentation of the ordered spinel structure (*a*), tetrahedra in the ordered spinel structure (*b*), and two types of octahedra (dark and dashed) in the ordered spinel structure (*c*).

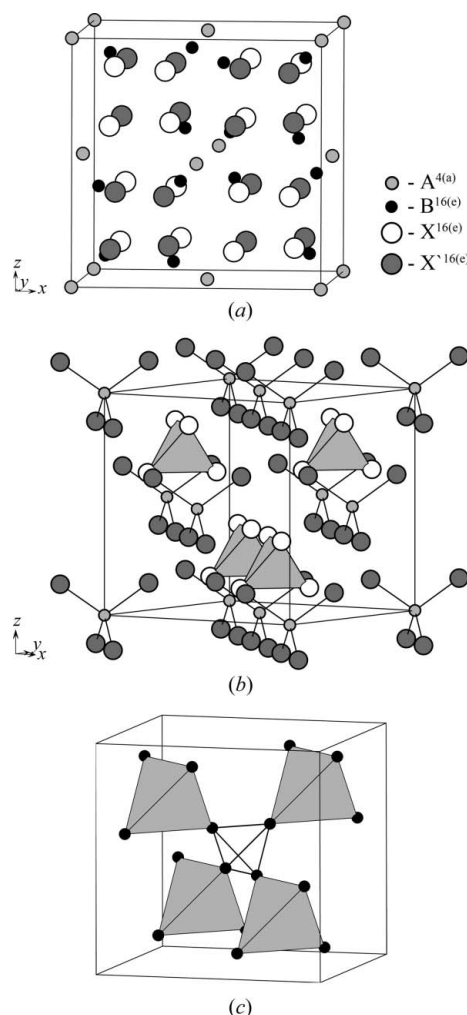


Figure 7
Calculated low-symmetry anion-ordered spinel structure with space group $F\bar{4}3m$ and structural formula $A^{4a}B_4^{16e}X_4^{16e}X_4'^{16e}$. Atom presentation of the ordered spinel structure (*a*), tetrahedra in the ordered spinel structure (*b*), B^{16e} metallic tetrahedra (*c*). A substance with composition $\text{Re}_4\text{As}_6\text{S}_3$ has a similar structure. In this structure there are Re_4 clusters (Besnard *et al.*, 2003).

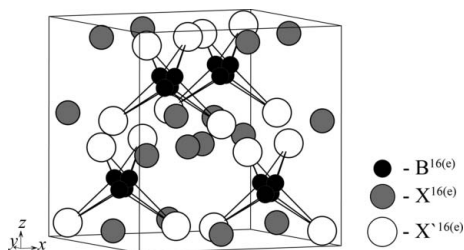


Figure 8
 Calculated low-symmetry anion-ordered spinel structure with space group $F\bar{4}3m$ and structural formula $B_4^{16e}X_4^{16e}X'^{16e}$. A substance with composition $\text{Re}_4\text{Te}_4\text{S}_4$ has a similar structure. In this structure there are Re_4 clusters (Fedorov *et al.*, 1994, 1996).

the features of the structure of the $R\bar{3}2/m$ phases are shown. $\text{Ga}_3\text{O}_3\text{N}$ has this structure (Boyko *et al.*, 2011). This substance possesses unusual electronic properties. Boyko *et al.* (2011) considered three models of the $\text{Ga}_3\text{O}_3\text{N}$ structure, described by space groups $Ima2$, $Imm2$ and $R\bar{3}2/m$. Study of the local electronic structure of this substance allowed the authors to establish the ordered arrangement of anions and to choose the model of the structure with space group $R\bar{3}2/m$. It should be noted that, according to our theory, at the formation of the $R\bar{3}2/m$ -phase structure, not only oxygen and

nitrogen ordering occurs, but also ordering of two of the three atoms of gallium, located in positions $1a$ and $3d$, takes place. The structural formula of $\text{Ga}_3\text{O}_3\text{N}$ should be $\text{Ga}_1^{1a}\text{Ga}_3^{3d}\text{Ga}_2^{2c}\text{N}^{2e}\text{O}_6^{6h}$.

Ordered spinel structure with enantiomorphic space groups $P4_12_12$ and $P4_32_12$. The critical irrep inducing $P4_12_12$ - and $P4_32_12$ -phase formation is the six-dimensional representation $\mathbf{k}_{10}(\tau_2)$. It can be shown that the structures of these phases are formed as a result of displacements of all atom types and also by ordering of atoms located in positions $32e$ of the spinel structure (the type of order is 1:1). The structural formula of the low-symmetry phase should be $A^{4a}B_2^{8b}X_2^{8b}X_2^{8b}$. The features of the $P4_12_12$ and $P4_32_12$ structures are given in Fig. 10. An example of this structure is that of MgTi_2O_4 (Isobe & Ueda, 2002; Schmidt *et al.*, 2004). In this substance at a temperature of ~ 260 K a phase transition occurs, accompanied by formation of tetragonal spinel modifications with space groups $P4_12_12$ and $P4_32_12$ (Isobe & Ueda, 2002; Schmidt *et al.*, 2004). High-resolution synchrotron and neutron powder diffraction and also X-ray investigation shows the existence of weak superstructure reflections (Schmidt *et al.*, 2004). According to our calculations these reflections are caused by ordering of oxygen ions (Fig. 10) (Talanov *et al.*, 2012). The theory predicts that ordering of oxygen ions should be of the

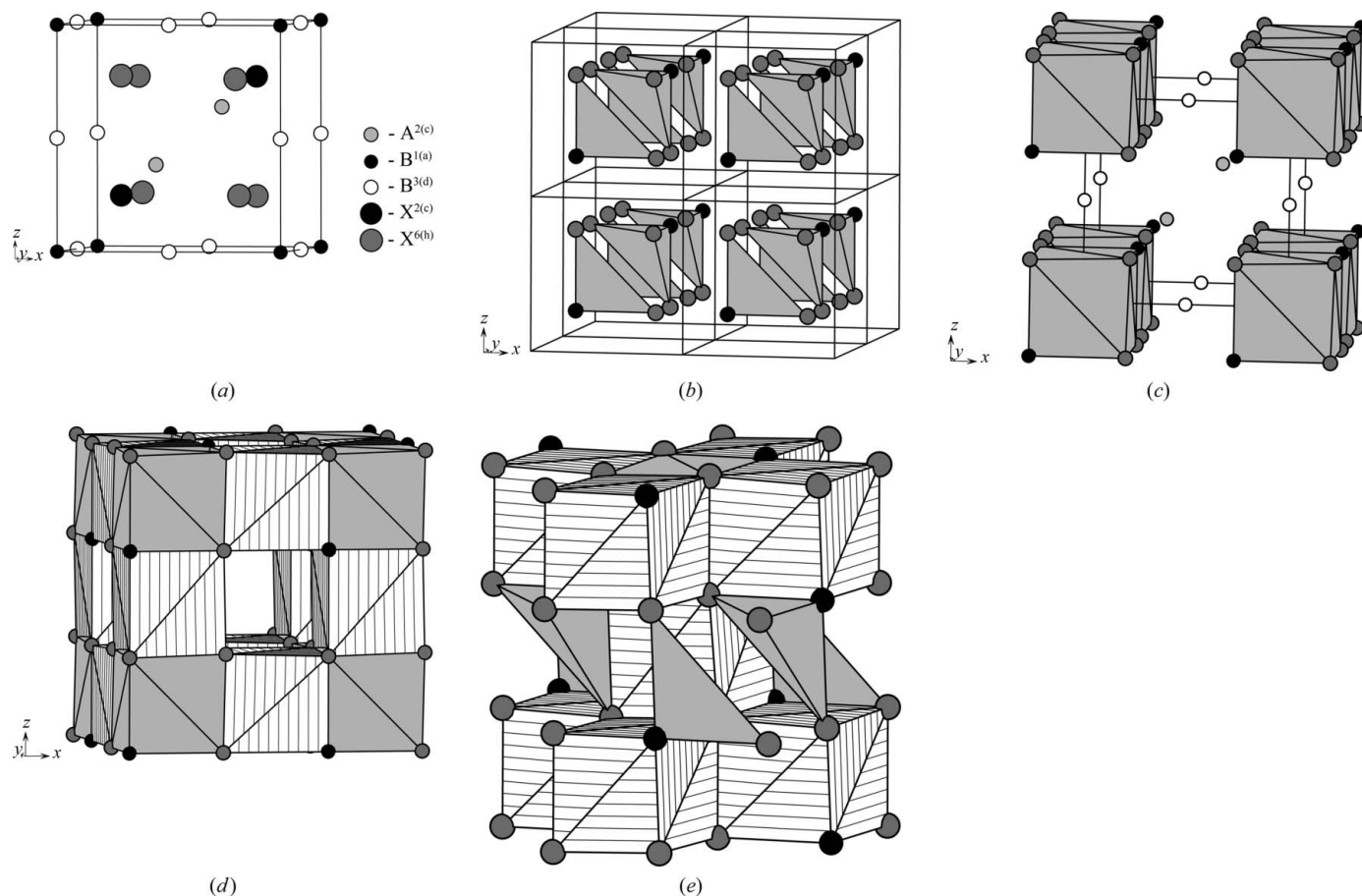


Figure 9
 Calculated low-symmetry ordered spinel with space group $R\bar{3}2/m$. Atom presentation of the ordered spinel structure (a); tetrahedra $[A^{2c}X^{2c}X_6^{6h}]$ in the ordered spinel structure (b); distorted hexahedra $[X_2^{2c}X_6^{6h}]$ with the central atom B^{1a} (c); distorted hexahedra $[X_2^{2c}X_6^{6h}]$ with the central atom B^{3d} and tetrahedra $[A^{2c}X^{2c}X_3^3]$ (d); and hexahedral presentation of the ordered spinel structure (e).

1:1 type. The symmetry of the order parameter, and the thermodynamics and mechanisms of formation of the atomic and orbital structure of the low-symmetry ordered MgTi_2O_4 spinel modification have been studied (Talanov *et al.*, 2012).

7.4. Atom ordering in two sublattices

One type of superstructure with simultaneous cation ordering in spinel structure positions $8a$ and $16d$ is known. It is an ordered phase of $\text{LiZn}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with space group $P2_13$. This phase is formed by two order parameters: $(\xi)^4$ and $(0, \varphi, 0, \varphi, 0, -\varphi)^1$. These two irreps form a point group of order 192 in the seven-dimensional space of the order parameter. The structural mechanism of the low-symmetry phase formation is defined by representation $\mathbf{k}_{10}(\tau_3) + \mathbf{k}_{11}(\tau_4)$. It appears to be complex and includes: (i) binary cation ordering of the 1:1

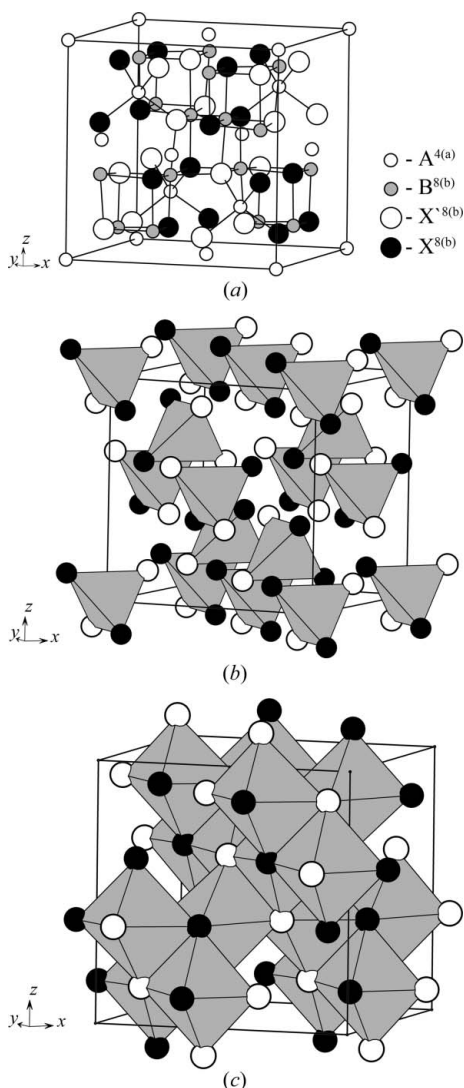


Figure 10 Calculated low-symmetry ordered structure of the tetragonal spinel modification of MgTi_2O_4 (on the basis of the cubic initial spinel structure). Atom presentation of the ordered spinel structure (a), tetrahedra arrangements in the ordered tetragonal spinel structure (b), and octahedra arrangements in the ordered tetragonal spinel structure (c).

type in tetrahedral spinel positions $8a$ and the 1:3 type in octahedral spinel positions $16d$; (ii) ordering of four anions of the 1:1:3:3 type in the initial spinel phase structure; and (iii) all types of atom displacements.

This structural mechanism of $P2_13$ -phase formation is much more complex than that proposed previously (Lee *et al.*, 2002). The calculated structural formula of the low-symmetry $P2_13$ phase should be $(A_{1/2}^{4a}A_{1/2}^{4a})[B_{1/2}^{4a}B_{3/2}^{12b}]X^{12b}X^{12b}X^{4a}X^{4a}$. Experimental data on the structure of $\text{LiZn}_{0.5}\text{Mn}_{1.5}\text{O}_4$, obtained by neutron diffraction and X-ray analyses, agree with the proposed structural formula (Lee *et al.*, 2002). The calculated structure of the $P2_13$ phase is shown in Fig. 11. The structural formula of $\text{LiZn}_{0.5}\text{Mn}_{1.5}\text{O}_4$ should be $(\text{Li}_{0.5}^{4a}\text{Zn}_{0.5}^{4a})[\text{Li}_{0.5}^{12b}\text{Mn}_{1.5}^{12b}]\text{O}^{12b}\text{O}^{12b}\text{O}^{4a}\text{O}^{4a}$. The symmetry of the order parameter, and the thermodynamics and mechanisms of formation of the atomic structure of the low-symmetry ordered cubic $\text{LiZn}_{0.5}\text{Mn}_{1.5}\text{O}_4$ oxide spinel have been studied by Talanov & Shirokov (2013).

8. Conclusions

The atomic ordering in the spinel structure was studied within a unified approach based on the Landau phenomenological phase-transition theory. Group-theoretical methods of the Landau theory were used to investigate the structures of ordered spinels. Based on the hypothesis of one critical representation, we established the order-parameter symmetry and the space groups of the low-symmetry spinel modifica-

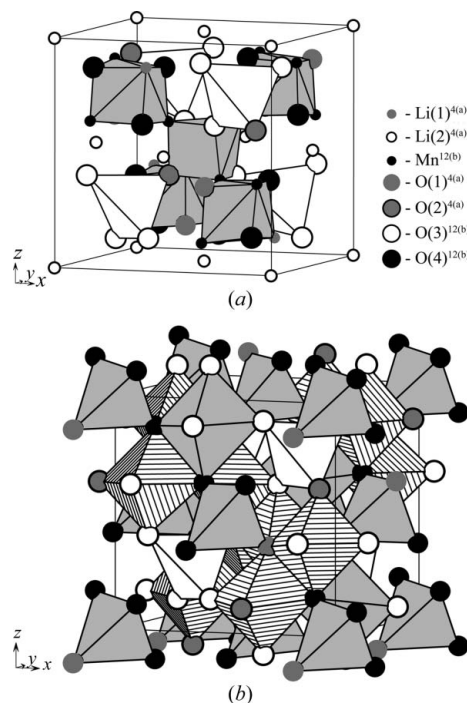


Figure 11 Fragments of the calculated low-symmetry ordered structure of $\text{LiZn}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Atom presentation of the ordered spinel structure (zinc ions are not shown) (a) and tetrahedra and octahedra in the ordered spinel structure (b). In (b) two types of octahedra (octahedra with central ions Mn^{12b} are dashed, octahedra with central ions Li^{4a} are grey) are shown.

tions, and calculated the stratification of Wyckoff positions 8a, 16d and 32e of the initial high-symmetry phase with a spinel structure at the transition to the low-symmetry phases. The possibility of the existence of 305 phases with different types of order in position 8a (including seven binary and seven ternary cation substructures), 537 phases in position 16d (including eight binary and 11 ternary cation substructures), 595 phases in position 32e (including seven binary and four ternary anion substructures) and 549 phases with simultaneous ordering in positions 8a and 16d (including five substructures with binary order in tetrahedral and octahedral sublattices, two substructures with ternary order in both spinel sublattices, and nine substructures with different combined types of binary and ternary order) was determined. The structural mechanisms of forming ordered spinel phases were considered. Calculated structures of the spread types of ordered low-symmetry spinel modifications were given.

Comparison of theoretical results and experimental data was made. The absolute part of the experimentally studied superstructures with binary atom ordering agrees with the theoretical results of this work.

Thus, in this work all possible types of binary and ternary ordering of cations and anions in the spinel structure have been determined. We hope that the data of Tables 1–4 will be helpful in research on the structures of new spinels and their low-symmetry modifications.

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