

phys. stat. sol. (b) **162**, 339 (1990)

Subject classification: 61.60; S11.2

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## Structural Modelling of Low-Symmetry Phases of Spinel

### II. Phases with 1 : 3 Octahedral Order <sup>2)</sup>

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On the basis of the phenomenological theory of phase transitions the structural mechanism of ordering of octahedral cations of the type 1 : 3 in spinels is studied. With the help of the basic functions of the active six-dimensional irreducible representations of the group  $Fd3m$  the structure of the ordered phase is deduced theoretically from the non-ordered phase. The qualitative pictures of possible displacements of atoms near the temperature of the phase transition are given. The existence of isostructural modifications of the ordered structure is predicted.

Auf Grund der phänomenologischen Theorie des Phasenübergangs wird der Strukturmechanismus der Anordnung von oktaedrischen Kationen vom 1 : 3-Typ in Spinellstrukturen untersucht. Mit Hilfe von Basisfunktionen der sechsdimensionalen irreduziblen Darstellung der  $Fd3m$ -Gruppe wird die Struktur einer geordneten Phase aus einer ungeordneten theoretisch abgeleitet. Qualitative Bilder möglicher Verschiebungen von Atomen in der Nähe der Temperatur des Phasenübergangs werden angeführt. Die Existenz von isostrukturellen Modifikationen der geordneten Struktur wird vorhergesagt.

### 1. Introduction

In chemical compounds with spinel structure (space group  $Fd3m$ ) cations occupy two non-equivalent crystallographic sublattices tetrahedral (8(a)) and octahedral (16(d)). If at least one of these sublattices is occupied by more than one kind of cations, a superstructure can be formed. Numerous ordered spinels with different types of long-range order have been found experimentally [1]. In the octahedral sublattice three types of ordering are most wide-spread, which correspond to ratios of cation numbers 1 : 3 and 1 : 1 (two different superstructures correspond to the latter case). The aim of this work is to find out the mechanism of formation of spinel compounds with the order 1 : 3 in the octahedral sublattice from the non-ordered structure. This task presents interest in many respects. In particular, the following moments should be noted. In the works of De Boer, Van Santen, and Verveij [2, 3] the gain in electrostatic energy at the formation of different types of superstructures is computed. The energy of ordering of cations, for example, for lithium ferrite  $LiFe_5O_8$  appeared to be equal to 474.2 kJ/mol. This value by several orders exceeds the thermal energy at the temperature of the phase transition. Actually, the latent heat of transformation for the temperature  $T_c = 1020$  K is only 8.4 kJ/mol [2]. Such a considerable discrepancy of the given values (energy paradoxon) proves the existence of compensative processes, which take place simultaneously with ordering of cations. Usually it is supposed that after destroying the state with long-range order short-range order is preserved; the difference

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between the energy of both ordering types being very insignificant [3, 4]. This explanation is founded on the well-known Anderson result, which demonstrated that in the octahedral lattice of spinels it is possible to reach perfect short-range order [5]. However, the discrepancy marked above can be observed not only for spinels, but for other structure types too, as, e.g., for perovskites [6, 7] not having specific sublattices. In our opinion, one of the compensative processes, which accompany ordering of cations, can be lattice reconstruction, connected with displacements of cations and anions. The method of computation of the structural mechanism of phase transitions has been considered in the first part of this paper. Here we describe in detail the scheme of finding the possible types of ordered phases of the crystal.

## 2. The Method of Computation of the Ordered Phase

Among phase transitions of ordering type it is possible to single out a large class of second-order transformations. Powerful group-theoretical methods were developed for this class, which go back in their basis to classical works of Landau and Lifshitz [8]. Two important propositions are well-grounded in these works, the so-called conception of one irreducible representation (IR) and the Lifshitz criterion, which singles out only transitions in proportionate crystal structures, stable to long-wave space modulations. These propositions allow to distinctly limit the number of geometrically possible dissymmetric phases at the second-order phase transitions. These propositions can be applied also to a considerable number of first-order phase transitions "close" to the second-order type [9].

Let us consider a phase transition from the initial non-ordered phase with the space symmetry  $G$  into a dissymmetric ordered phase with the symmetry  $G_D$  ( $G_D$  is a subgroup of the group  $G$ ). As the result of such a transition of ordering type the orbit  $R$  of the group  $G$  is split into a number of different orbits  $R_D^i$  of the group  $G_D$ . In geometrical language it means that there occurs a kind of colouring (i.e. assigning of different scalar values) of earlier equivalent junctions of the orbit  $R$ . Formation of dissymmetric structure at phase transitions in Landau's theory can be described by some function  $\Delta\varrho(\mathbf{r})$ , for example, by the function of changing the temporal average of the electrical charge density. When considering transitions of the ordering type as  $\Delta\varrho(\mathbf{r})$  it is convenient to use the scalar function determined on the given equivalent positions (EP) and characterizing the colours of the EP points. To crystallographically equivalent junctions of the EP correspond equal values  $\Delta\varrho(\mathbf{r})$ . Knowing the type of splitting of the orbit  $R$  into orbits  $R_D^i$ , it is possible to find the ratios of the numbers of different junctions in the dissymmetric phase. These ratios determine the possible chemical composition in the given  $R$  supposing that in every orbit  $R_D^i$  there is one kind of atoms, the kinds of atoms being different for different orbits.

To find the splitting of  $R$  at the second-order phase transitions or at the first-order phase transitions "close" to the second-order ones we used the group-theoretical method described in [10 to 12]. In [10] all the possible symmetry groups of dissymmetric phases are found, induced by every representation of the group  $G = Fd3m$ , satisfying the Lifshitz criterion. For every  $G_D$  the so-called stationary vector  $C = \{C_1, \dots, C_n\}$  corresponding to it is pointed out which determines the concrete kind of the parameter order being transformed by the  $n$ -dimensional IR. In [12] scalar basis functions of small IR of the group  $Fd3m$  are built. With their help by standard methods scalar basis functions of the full IR of the group

$Fd3m$  are built. For building the function  $\Delta\varrho = \sum_{i=1}^n C_i \varphi_i$ , which determines the "colours"

Table 1  
Binary superstructures in spinels

site	critical IR	$G_D$	type of order	$V'/V$	stationary vector
8(a)	11-4	$F\bar{4}3m$	1:1	1	$C$
8(a)	9-1	$R\bar{3}m$	1:1	2	$C000$
8(a)	9-4	$R\bar{3}m$	1:1	2	$C000$
16(d)	11-7	$Jmma$	1:1	1	$C00$
16(d)	11-7	$R\bar{3}m$	1:3	1	$CCC$
16(d)	10-3	$P4_132$	1:3	4	$C0C0C0$
16(d)	10-3	$P4_332$	1:3	4	$0C0C0C$
16(d)	10-3	$P4_122$	1:1	2	$C00000$
16(d)	10-3	$P4_322$	1:1	2	$0C0000$
16(d)	9-4	$F\bar{4}3m$	1:1	8	$CCCC$
32(e)	11-4	$F\bar{4}3m$	1:1	1	$C$
32(e)	11-7	$R\bar{3}m$	1:3	1	$CCC$
32(e)	11-7	$Jmma$	1:1	1	$C00$
32(e)	11-10	$J4_1md$	1:1	1	$C00$
32(e)	10-3	$P4_132$	1:3	4	$C0C0C0$
32(e)	10-3	$P4_332$	1:3	4	$0C0C0C$
32(e)	10-3	$P4_122$	1:1	2	$C00000$
32(e)	10-3	$P4_322$	1:1	2	$0C0000$
32(e)	10-4	$P4_12_12$	1:1	2	$C00000$
32(e)	10-4	$P4_32_12$	1:1	2	$0C0000$

Note:  $V'/V$  means variation in the volume of the primitive cell.

of the points of the orbit  $R$ , it is enough to compute a linear combination of components of the parameter of the order  $C_i$  and the basis function  $\varphi_i$  of the corresponding full IR.

It should be noted that not all the IR of the group  $G$  can lead to transitions of the ordering type, but only those which come into the so-called transpositional representation, realized on the considered orbit  $R$ . For the orbit 8(a) these are only IR 11-4, 9-1, 9-4; for the orbit 16(d) 11-7, 10-3, 9-1, 9-4, 9-5; for the orbit 32(e) 11-4, 11-7, 11-10, 10-3, 10-4, 9-1, 9-4. The number of IR is pre-set by two quantities: the first one points out to the wave vector  $K$  (in correspondence with [13]), the second one to the ordinal number of the group representation of this wave vector. In Table 1 all possible types of phases induced by one IR  $G_0 = Fd3m$  and characterized by the binary order of atoms are listed [14, 15].

### 3. The Structural Mechanism and Its Discussion

Ordered crystals of the general formula  $AB_{1/2}B_{3/2}X_4$  have the space group  $P4_332$  or  $P4_132$  [16].

Among the symmetry elements of the space group in the ordered phase there are no inversion and reflections, but only symmetry axes. These crystals can exist in right-handed and left-handed forms, which are mirror reflections of each other. The phases with symmetries  $P4_232$  and  $P4_132$  are enantiomorphous modifications.

The structure of the ordered modification of the spinel is determined by all the possible rearrangements of atoms in the non-ordered phase and by their displacements. In immediate

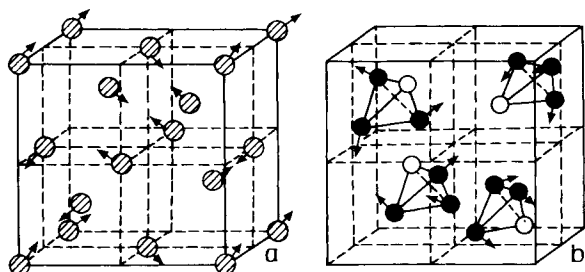


Fig. 1. The qualitative picture of displacements of tetrahedral and octahedral cations at formation of the ordered phase, hatched circles A,  $\circ$  B(4b),  $\bullet$  B(12(d))

proximity to the phase transition point it is possible to ignore the role of non-critical coordinates of a crystal. With moving away from this points their role evidently increases and they may turn to be essential in the analysis of the data of X-ray structural and neutronographic experiments [11].

The active IR 10–3 enters the transpositional as well as the mechanical representations [12], so reduction of symmetry may be caused by the two mechanisms simultaneously (Fig. 1 to 5).

Simultaneously with ordering of cations in the octahedral sublattice there takes place ordering of junctions in the anion sublattice. If anions are formed by one and the same chemical element, they become crystallographically non-equivalent in the low-symmetric phase. Their type of ordering is 1 : 3; they are split into two groups, to each of these groups it is possible to attribute its "colour".

When the ordered phase is being formed, there occurs displacement of tetrahedral and octahedral cations as well as of anions. The tetrahedral sublattice in the structure of the non-ordered spinel is identical to the diamond structure. Cations displace in such a way that in the ordered phase they take monovariant position 8(c) with their own trigonal symmetry 3 ( $C_3$ ). Cations occupying the corners of the cube and the centres of its facets displace to meet cations located inside the octants (Fig. 1a). The octahedral cations are divided into two groups. Calculation proves that cations with "white colour" (white circles

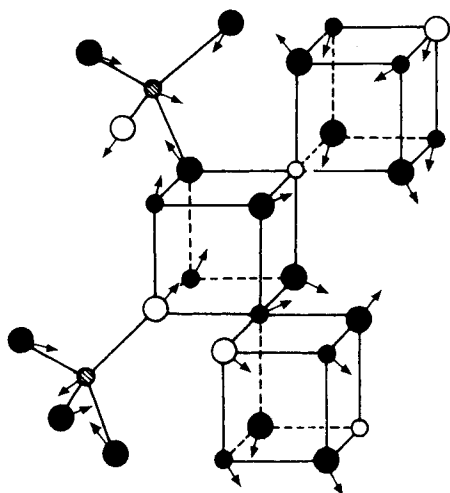


Fig. 2. A fragment of the spinel structure  $\circ$  X(8(c)),  $\bullet$  X(24(c)), hatched circles A(8(c)). Projection of octahedral atoms onto the plane (001)

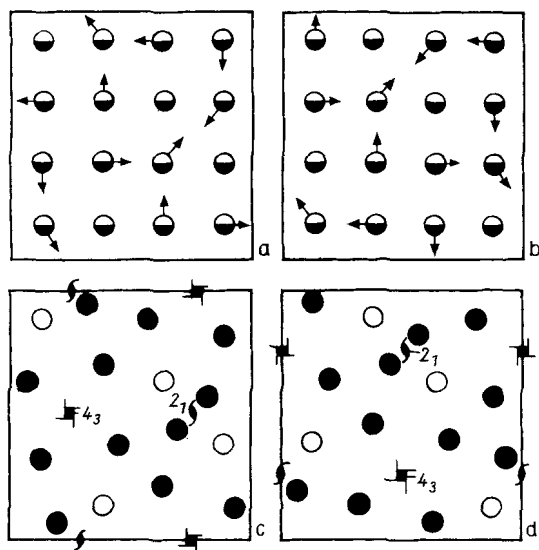


Fig. 3. Displacement of octahedral cations (a, b) leading to the formation of the phases  $P4_332$  (c) and  $P4_132$  (d).  $B(4b)$  —  $\circ$ ,  $B(12d)$  —  $\bullet$

in Fig. 1b) do not displace at all (there are four such cations in an elementary cell); they occupy the invariant (i.e. not having free parameters) position 4(b) with their own trigonal symmetry 32 ( $D_3$ ). The other group of octahedral cations (black circles in Fig. 1b) after displacement occupy the monovariant EP 12(d) with its own monoclinic symmetry 2 ( $C_2$ ). In the position 32(e) IR 10-3 comes into the mechanical representation three times. In this

case the basis functions do not have the meaning of real critical displacements of atoms, i.e. with the help of symmetry methods the dynamic matrix of the crystal is not fully diagonalized. Real displacements turn out to be linear combinations of all basis functions, and the coefficients of displacement depend on the microscopic characteristics of chemical relations in the crystal. Displacements of anions are also of two types. Anions with "white colour" have only one specific direction of displacement: they

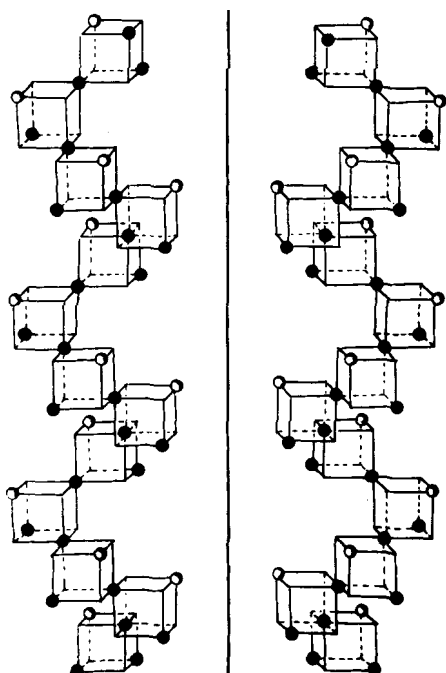


Fig. 4. Cation spirals in the ordered enantiomorphous modifications of spinel (results of computation). The spirals in the enantiomorphous modifications are "mirror" reflections. The line is the conventional designation of the mirror

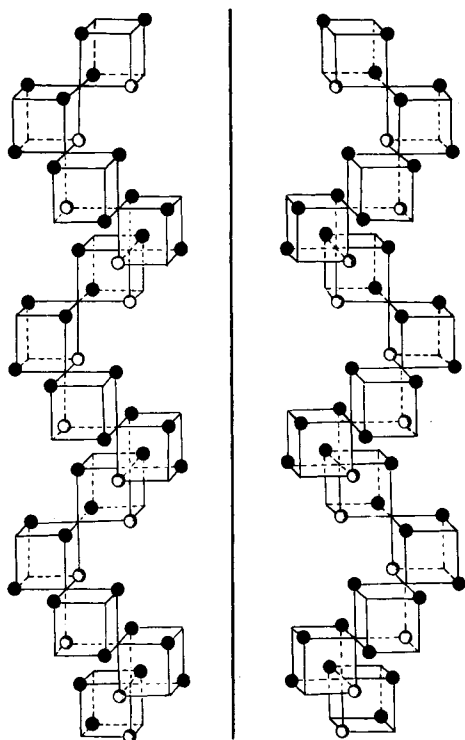
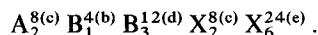


Fig. 5. Anion spirals in the ordered enantiomorphous modifications of spinel (result of computation). The line is the conventional designation of the mirror

occupy monovariant position 8(c) with their own symmetry 3 ( $C_3$ ). Anions with "black colour" form the common EP 24(e); their position in the lattice is described by three "gliding" parameters. The own symmetry of the position is triclinic 1 ( $C_1$ ) (Fig. 2). Thus, the structural formula of the fully ordered spinel looks as follows:



The EP obtained by computation of the ordered spinel are in conformity with the data of X-ray structural and neutronographic research [16, 17, 18]. Parameters describing displacements of atoms may have different signs. Depending on the signs of

parameters isostructural modifications of the ordered structure are possible. Isostructural phase transitions may take place [19 to 21].

The symmetry of the ordered phases is described by two space groups. This is connected with the fact that among the symmetry elements there are screw axes of different signs, for example: either axes  $4_1$  or only axes  $4_3$ .

The corresponding space groups are isomorphous.

Crystal structures which are described by such groups are equal, however, it is possible to match them only by means of reflection in the symmetry plane. The structure with the space group  $P4_332$  (Fig. 6) has left-hand screw axes, and the structure with the space group

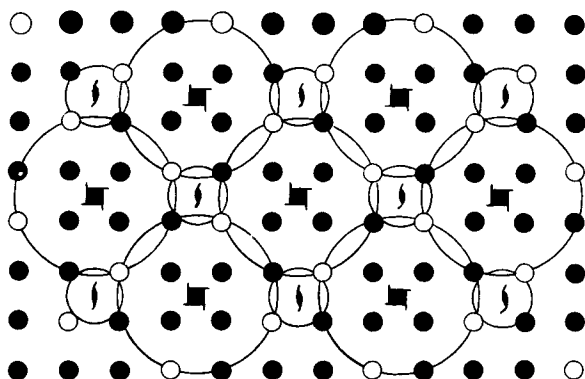


Fig. 6. Projection of the octahedral atoms onto the (001) plane for the modification with the space group  $P4_332$ . Displacements of atoms are not indicated. Projections of B(4(b)) spirals along crystallographic screw operations are shown.  $\circ$  B(4(b)),  $\bullet$  B(12(d))

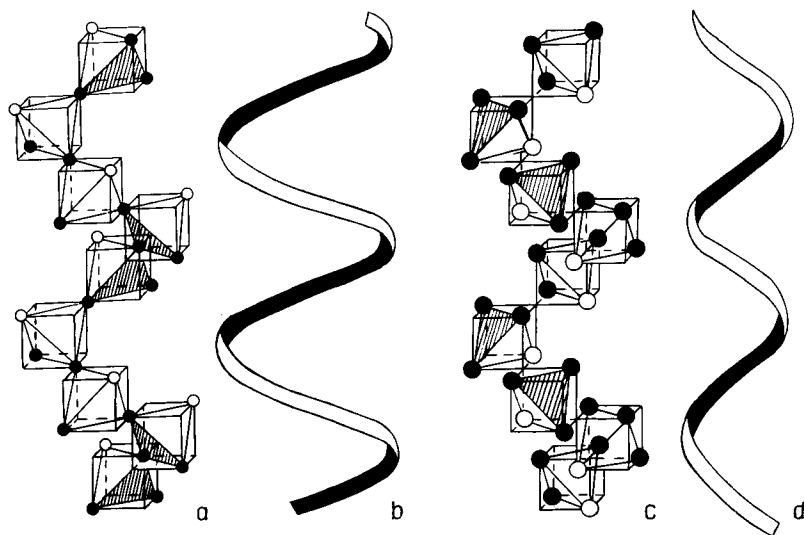


Fig. 7. a) B-cation and c) X-anion (c) spirals and their conventional designation b) and d)

$P4_132$  right-hand screw axes. At the left-hand screw movement along the axis perpendicular to Fig. 6 with clockwise rotation we get the axis  $4_3$ . By analogy, at the right-hand screw movement we get the axis  $4_1$ . The characteristic feature of the structures enantiomorphous

modifications of spinels is the existence of cation-anion spirals (Fig. 4, 5, to 7). In order to show the peculiarities of the spiral topology the tetrahedron edges lying opposite to atoms with “white colour” are given in dashed lines. The darkened sides of the spirals correspond to them (Fig. 7 (b, d)). (B(4b)) cation and (X(8c)) anion spirals form a double spiral (Fig. 8). The external spiral in Fig. 8 is the cation one, and the internal one is the anion spiral. In real samples of ordered spinels both enantiomorphous modifications may be found simultaneously [22, 23]. It seems to be connected with the

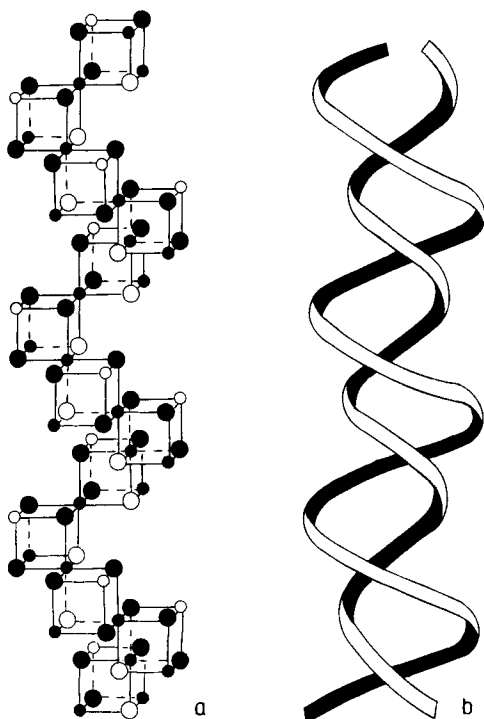


Fig. 8. Double spiral in the structure of the ordered spinel with the space group  $P4_132$  consisting of B(4b)-cation and X(8c)-anion spiral: a) atom representation, b) spiral representation

structural compensation effect: at the second-order phase transitions and the first-order ones "close" to them the structure of the low-symmetrical modification "counteracts" the change of symmetry and structural type [23, 24]. The existence of screw axes of different signs in two enantiomorphous modifications leads to the fact that on the average the symmetry of a crystal does not change as a result of the phase transition.

#### 4. Conclusion

Thus, formation of the cation superstructure of the type 1:3 in octahedral junctions of spinels has a complex structural mechanism: it is accompanied by the ordering of junctions in the anion sublattice of the crystal and also by displacements of cations and anions. The group-theoretical method used in is effective in studying the structural mechanisms of formation of the ordered phases.

#### Acknowledgements

I would like to thank Prof. P. Tarte (Belgium), Prof. V. C. Joubert (France), Prof. A. Navrotsky (USA) for sending me the reprints of their classical works.

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(Received July 10, 1990)