



Cite this: *Phys. Chem. Chem. Phys.*,  
2016, **18**, 10600

# Phenomenological thermodynamics and the structure formation mechanism of the $\text{CuTi}_2\text{S}_4$ rhombohedral phase

Michail V. Talanov,<sup>\*a</sup> Vladimir B. Shirokov<sup>ab</sup> and Valery M. Talanov<sup>c</sup>

The theory of structural phase transition in  $\text{CuTi}_2\text{S}_4$  is proposed. The symmetry of order parameters, thermodynamics and the mechanism of the atomic structure formation of the rhombohedral Cu–Ti–thiospinel have been studied. The critical order parameter inducing the phase transition has been found. Within the Landau theory of phase transitions, it is shown that the phase state may change from the high-symmetry cubic disordered  $Fd\bar{3}m$  phase to the low-symmetry ordered rhombohedral  $R\bar{3}m$  phase as a result of phase transition of the first order close to the second order. It is shown that the rhombohedral structure of  $\text{CuTi}_2\text{S}_4$  is formed as a result of the displacements of all types of atoms and the ordering of Cu-atoms (1:1 order type in tetrahedral spinel sites), Ti-atoms (1:1:6 order type in octahedral spinel sites), and S-atoms (1:1:3:3 order type). The Cu- and Ti-atoms form metal nanoclusters which are named a “bunch” of dimers. The “bunch” of dimers in  $\text{CuTi}_2\text{S}_4$  is a new type of self-organization of atoms in frustrated spinel-like structures. It is shown that Ti-atoms also form other types of metal nanoclusters: trimers and tetrahedra.

Received 18th January 2016,  
Accepted 19th February 2016

DOI: 10.1039/c6cp00387g

www.rsc.org/pccp

## 1. Introduction

Copper-containing thiospinels exhibit a wide variety of physical properties that make them interesting from a scientific point of view.<sup>1–3</sup> For example, large negative magnetoresistance is observed in the ferromagnetic thiospinel compound  $\text{CuCrZrS}_4$ .<sup>4</sup> The other spinels  $\text{CuRh}_2\text{S}_4$  and  $\text{CuRh}_2\text{Se}_4$  are superconductors.<sup>5–9</sup> It is interesting to note that  $\text{CuRh}_2\text{S}_4$  is the first compound with the pressure-induced superconductor–insulator transition, which occurs between 5.0 and 5.6 GPa.<sup>10</sup> The iridium thiospinel  $\text{CuIr}_2\text{S}_4$  shows a temperature-induced metal–insulator transition with simultaneous charge ordering and spin dimerization transition which is a rare phenomenon in three-dimensional compounds.<sup>11–14</sup>

Among copper-thiospinels,  $\text{CuTi}_2\text{S}_4$  has attracted great interest due to the metallic behavior and the weak magnetism of both Cu ions at the tetrahedral A-site and Ti ions at the octahedral B-site. The strong crystal field scheme leads the ground state of  $\text{Cu}^{2+}$  and  $\text{Ti}^{3+}$  to  $(e_g)^4(t_{2g})^5$  ( $S = 0$ ) and  $(t_{2g})^1$  ( $S = 1/2$ ) electronic configurations, respectively.<sup>15</sup> Below 5 K, the copper-thiospinel transforms into a spin singlet state.<sup>15</sup> The cubic thiospinel  $\text{CuTi}_2\text{S}_4$  can be formally described in another way as  $\text{Cu}^+\text{Ti}^{3+}\text{Ti}^{4+}\text{S}_4$  with non-magnetic  $\text{Cu}^+$  and mixed-valence Ti ( $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$ ).<sup>1</sup> The electronic,

magnetic and structural properties of this compound are, however, not sufficiently understood at present.

There is another reason for having interest in  $\text{CuTi}_2\text{S}_4$ : in three dimensional geometrically frustrated magnets with two-dimensional kagome-layers and triangular-sublattices, there has been a recent focus on the presence of a quantum spin liquid and/or heavy fermion-like states. It is assumed that such situation is realized in  $\text{CuTi}_2\text{S}_4$ .<sup>16</sup>

The structure of  $\text{CuTi}_2\text{S}_4$  depends on the method of synthesis. According to ref. 17 the  $\text{CuTi}_2\text{S}_4$  compound has a normal spinel structure at room temperature, where Cu ions occupy the tetrahedral site and Ti ions occupy the octahedral site, which crystallize into a cubic  $Fd\bar{3}m$  structure.  $\text{CuTi}_2\text{S}_4$  shows the Pauli paramagnetism, and there is no structural phase transition down to 8.3 K.<sup>17</sup> Hence, according to ref. 18  $\text{CuTi}_2\text{S}_4$  has the low-symmetry rhombohedral spinel modification with the centrosymmetric space group  $R\bar{3}m$  which is irreversibly transformed into the cubic spinel at temperatures above 450 °C.<sup>18</sup> Kinetically stabilized and rhombohedrally modified  $\text{CuTi}_2\text{S}_4$  has been synthesized by the reaction of the constituent elements using eutectic alkali metal halide fluxes.<sup>18</sup> According to the electronic structure calculation based on the density functional theory the rhombohedral thiospinel is energetically preferred, with a lower total energy of 1.6 eV per formula unit.<sup>18</sup>

However, this rhombohedral modification of  $\text{CuTi}_2\text{S}_4$  arouses scientific interest not only as a material with promising physical properties, but also as a crystal with a possible unique structure and electronic organization explained in this thesis. The structure of  $R\bar{3}m$ -modification of  $\text{CuTi}_2\text{S}_4$  has atom distribution on

<sup>a</sup> South Federal University, Rostov-on-Don, Russia. E-mail: tmikle-man@mail.ru

<sup>b</sup> South Scientific Center, Russian Academy of Sciences, 344006, Rostov-on-Don, Russia

<sup>c</sup> South Russia State Polytechnical University, Novocherkassk Polytechnical Institute, 346400, Novocherkassk, Russia. E-mail: valtalanov@mail.ru



**Table 1** Irreps of  $Fd\bar{3}m$  group symmetry induced low-symmetry rhombohedral  $R\bar{3}m$ -phases. Designations for order parameters:  $\mathbf{k}_9 - \eta$ ,  $\mathbf{k}_{10} - \varphi$ ,  $\mathbf{k}_{11} - \xi$ ,  $V/V_0$  is the change in the primitive cell volume as a result of the structural phase transition

Irreps	Order parameters	$V/V_0$	Stratification of the spinel Wyckoff positions in the $R\bar{3}m$ -low-symmetry phases		
			8a	16d	32e
$\mathbf{k}_{11}(\tau_7)$	$\xi \xi \xi$	1	1(16):3m	1(8):m + 1(24):2/m	1(16):3m + 1(48):m
$\mathbf{k}_{10}(\tau_1)$	$\varphi \varphi \varphi \varphi \varphi \varphi$	4	1(4):3m + 1(12):m + 1(12):m + 1(12):2	1(2):m + 1(6):2/m	1(4):3m + 3(12):m + 1(24):1
$\mathbf{k}_{10}(\tau_3)$	$\varphi \varphi \varphi \varphi \varphi \varphi$	4	1(4):3m + 1(12):m + 1(12):m + 1(12):2	1(2):m + 1(6):2/m	1(4):3m + 3(12):m + 1(24):1
$\mathbf{k}_9(\tau_1)$	0 $\eta \eta \eta$	8	2(2):3m + 2(6):m + 2(6):m + 1(12):1	2(1):m + 2(3):2/m	2(2):3m + 6(6):m + 2(12):1
$\mathbf{k}_9(\tau_1)$	$\eta$ 0 0 0	2	2(8):3m	1(8):m + 2(12):2/m	2(8):3m + 2(24):m
$\mathbf{k}_9(\tau_4)$	0 $\eta \eta \eta$	8	2(2):3m + 2(6):m	1(2):+3(6):m + 2(6):2	2(2):3m + 6(6):m + 2(12):1
$\mathbf{k}_9(\tau_4)$	0 0 0 $\eta$	2	2(8):3m	2(4):3m + 1(24):m	2(8):3m + 2(24):m

Wyckoff positions similar to atom distribution in the high-order structure of  $\text{AlV}_2\text{O}_4$ . This high-order structure comprises complex “molecular” clusters – V-heptamers.<sup>19</sup> Large building blocks such as V-heptamers are a consequence of cooperation between charge, spin and orbital degrees of freedom of the V ions.<sup>19,20</sup> Hence, it is not clear whether it is possible to expect the formation of unique Ti-heptamers (analogue of V-heptamers) in  $\text{CuTi}_2\text{S}_4$  rhombohedral modification as a result of the same type of self-organization of atoms, charges, spins and orbitals.

The purpose of this study was to reveal symmetry, structural, and thermodynamic features of the formation of the low-symmetry rhombohedral phase with unusual metal nanoclusters from the cubic  $\text{CuTi}_2\text{S}_4$ -phase with a spinel structure. In this paper, we have mainly focused on the self-organization of atoms. We are the first to study this question with the help of group-theoretical, thermodynamic and structural methods of the modern theory of phase transitions. These methods were described earlier in detail.<sup>21–29</sup> We have also checked the separate results obtained by our methods by means of the ISOTROPY program.<sup>30,31</sup> The problem of self-organization of charges, spins and orbitals in the  $R\bar{3}m$ -modification of  $\text{CuTi}_2\text{S}_4$  is supposed to be considered later.

## 2. Theory of the structural phase transition in $\text{CuTi}_2\text{S}_4$

### 2.1. Symmetry of the order parameter

Using the results of group-theoretical analysis of the phase transitions occurring according to one critical irreducible representation (irrep) in the group  $Fd\bar{3}m$ , which satisfy the Lifshitz criterion,<sup>32</sup> we find that the space group  $R\bar{3}m$  may be generated by three-dimensional irrep  $\mathbf{k}_{11}(\tau_7)(1)$  as well as two six-dimensional irreps  $\mathbf{k}_{10}(\tau_1)(4)$  and  $\mathbf{k}_{10}(\tau_3)(4)$  and two four-dimensional irreps  $\mathbf{k}_9(\tau_1)(8,2)$  and  $\mathbf{k}_9(\tau_4)(8,2)$ . The indexing of wave vectors and irreps is given according to Kovalev.<sup>33</sup>  $\mathbf{k}_j(\tau_i)$  – the star of wave vectors  $\mathbf{k}_j$ ,  $i$  – the number corresponding to irrep  $\tau$  for a given star  $\mathbf{j}$ . The multiplication

in the primitive cell volumes as a result of phase transitions from the high-symmetry  $Fd\bar{3}m$ -phase to the low-symmetry  $R\bar{3}m$ -phase is shown in parentheses.

The results of group-theoretical analysis show that only in the case of the phase generated by irrep  $\mathbf{k}_9(\tau_4)$  the calculated distribution of the atoms on Wyckoff positions of the  $R\bar{3}m$ -phase is consistent with experimental data<sup>18</sup> (Table 1). The expressions are explained in this table. For example, the record of 1(8):m + 1(24):2/m means that Wyckoff position 16d of the group  $Fd\bar{3}m$  in the low-symmetry phase with the space group  $R\bar{3}m$  stratifies into one eight-fold Wyckoff position with local symmetry m and one 24-fold Wyckoff position with local symmetry 2/m.

A decisive circumstance in the choice of critical irrep and low-symmetry solution in the description of phase transition in  $\text{CuTi}_2\text{S}_4$  is the experimentally established  $Z_B(R\bar{3}m) = 12$ , where  $Z_B$  is the number of formula units in the Bravais cell.<sup>18</sup> The basis vectors of the unit cell  $A_1, A_2, A_3$  of the rhombohedral  $R\bar{3}m$ -phase are connected with the basis vectors of the cubic spinel structure  $A_{1\text{sp}}, A_{2\text{sp}}, A_{3\text{sp}}$  by relations:  $A_1 = 1/2(A_{1\text{sp}} - A_{3\text{sp}})$ ,  $A_2 = 1/2(-A_{1\text{sp}} + A_{2\text{sp}})$ ,  $A_3 = 2(A_{1\text{sp}} + A_{2\text{sp}} + A_{3\text{sp}})$ . The primitive cubic cell of the spinel contains two formula units; therefore, the primitive cell volume for the rhombohedral phase is larger than the primitive-cell volume for the cubic spinel by a factor of 2, *i.e.* it contains four formula units. The results are as follows: for the space group  $Fd\bar{3}m$   $Z_P = 2$ ,  $Z_B = 8$  and for the space group  $R\bar{3}m$   $Z_P = 4$ ,  $Z_B = 12$ . Hereafter,  $Z_P$  is the number of formula units in the primitive cell. These theoretical results also are consistent with experimental data.<sup>18</sup>

Thus, the critical irrep inducing phase transition in  $\text{CuTi}_2\text{S}_4$  is the four-dimensional irrep of star  $\mathbf{k}_9(\tau_4)$ . Irrep  $\mathbf{k}_9(\tau_4)$  corresponds to irrep  $\mathbf{L}_2^-$  in notations of Stokes and Hatch, 2007. A one-parameter solution (0 0 0  $\eta$ ) corresponds to the experimentally established phase (Table 2).

The four-component order parameter (OP), transformed according to irrep  $\mathbf{k}_9(\tau_4)$  of  $Fd\bar{3}m$  group symmetry, forms a point group of order 384 in four-dimensional space. The OP transformation properties are given by the following generator matrices:

$$\begin{matrix} a_1 & a_2 & a_3 & (h_2|0) & (h_3|0) & (h_5|0) & (h_{13}|\tau\tau\tau) & (h_{25}|\tau\tau\tau) \\ \begin{pmatrix} -1 \\ -1 \\ 1 \\ 1 \end{pmatrix} & \begin{pmatrix} -1 \\ 1 \\ -1 \\ 1 \end{pmatrix} & \begin{pmatrix} -1 \\ 1 \\ 1 \\ -1 \end{pmatrix} & \begin{pmatrix} 1 & & & \\ & 1 & & \\ & & 1 & \\ & & & 1 \end{pmatrix} & \begin{pmatrix} 1 & & & \\ & 1 & & \\ & & 1 & \\ & & & 1 \end{pmatrix} & \begin{pmatrix} 1 & & & \\ & 1 & & \\ & & 1 & \\ & & & 1 \end{pmatrix} & \begin{pmatrix} -1 & & & \\ & 1 & & \\ & & 1 & \\ & & & 1 \end{pmatrix} & \begin{pmatrix} -1 \\ 1 \\ 1 \\ 1 \end{pmatrix} \end{matrix}, \quad (1)$$



**Table 2** Low-symmetry crystal phases induced by irrep  $\mathbf{k}_9(\tau_4)$  of the space group  $Fd\bar{3}m$ . The superscript index in the structural formula means the type of Wyckoff position according to international tables for crystallography

No.	Order parameter	Symbol of space group	$V/V_0$	Translations of primitive cell of spinel structure	Structural formula
1	(0 0 $\eta$ $\eta$ )	$Cmcm$ (N63)	4	$2a_2 + 2a_3 - 2a_1, 2a_3 + 2a_1 - 2a_2,$ $2a_1 + 2a_2 - 2a_3$	$(Ac)^2A^g_2(B^g_2)^2B^f_2B^c_2(X^g_2)^4(X^f_2)^2X^h$
2	( $\eta$ $\eta$ $\eta$ $\eta$ )	$F\bar{4}3m$ (N216)	8	$2a_2 + 2a_3 - 2a_1, 2a_3 + 2a_1 - 2a_2,$ $2a_1 + 2a_2 - 2a_3$	$A^a(A^c_4)^2A^g_6A^b(B^e_4)^2(B^h_{12})^2(X^e_4)^4(X^h_{12})^4$
3	(0 0 0 $\eta$ )	$R\bar{3}m$ (N166)	2	$a_2 - a_1, a_1, 2a_1 + 2a_2 + 2a_3$	$(Ac_{1/2})^2B^a_{1/4}B^b_{1/4}B^h_{3/2}(X^c_{1/2})^2(X^h_{3/2})^2$
4	(0 $\eta$ $\eta$ $\eta$ )	$R\bar{3}m$ (N166)	8	$2a_3, -2a_2, 6a_2 - 2a_1 - 2a_3$	$(Ac_{1/8})^2(A^h_{3/8})^2(B^h_{3/8})^3B^c_{1/8}B^g_{3/8}B^f_{3/8}(X^h_{3/8})^6X^c_{1/8}X^c_{3/8}(X^i_{6/8})^2$
5	(0 $\eta_1$ $\eta_1$ $\eta_2$ )	$C2/m$ (N12)	8	$4a_2 - 2a_3, 2a_3, 2a_1 - 2a_2$	$(A_{1/8})^4(A^d_{2/8})^2(B^j_{2/8})^4(B^i_{1/8})^4B^h_{1/8}B^g_{1/8}(X^d_{2/8})^{12}(X^i_{1/8})^8$
6	( $\eta_1$ $\eta_2$ $\eta_2$ $\eta_2$ )	$R3m$ (N160)	8	$2a_1, 2a_1 - 2a_3, 6a_2 - 2a_1 - 2a_3$	$(Aa_{1/16})^4(A^b_{3/16})^4(B^b_{3/16})^6(B^a_{1/16})^2(B^c_{6/16})^2(X^b_{3/16})^{12}(X^a_{1/16})^4(X^c_{6/16})^4$
7	( $\eta_1$ $\eta_1$ $\eta_2$ $\eta_2$ )	$Imm2$ (N44)	8	$2a_3, 2a_1 - 2a_2, 2a_1 + 2a_2 - 2a_3$	$(Aa_{1/16})^2(A^c_{2/16})^2(A^c_{4/16})^2(A^d_{2/16})^2(A^b_{1/16})^2(B^c_{2/16})^4(B^d_{2/16})^4(B^e_{4/16})^4$ $(X^c_{2/16})^8(X^d_{2/16})^8(X^e_{4/16})^8$
8	(0 0 $\eta_1$ $\eta_2$ )	$C2_1/m$ (N11)	4	$a_1 + a_2, a_2 - a_1, 2a_3 - a_1 - a_2$	$(Ac_{1/4})^4(B^c_{1/4})^4(B^d_{2/4})^2(X^c_{1/4})^8(X^f_{2/4})^4$
9	( $\eta_1$ $\eta_2$ $\eta_2$ $\eta_3$ )	$Cm$ (N8)	8	$4a_2 - 2a_3, 2a_3, 2a_1 - 2a_2$	$(Aa_{1/16})^8(A^b_{2/16})^4(B^b_{2/16})^{12}(B^a_{1/16})^8(X^b_{2/16})^{24}(X^a_{1/16})^{16}$
10	(0 $\eta_1$ $\eta_2$ $\eta_3$ )	$Pi$ (N2)	8	$2a_1, 2a_2, 2a_3$	$(A_{1/8})^8(B^i_{1/8})^{16}(X^i_{1/8})^{32}$
11	( $\eta_1$ $\eta_2$ $\eta_3$ $\eta_4$ )	$P1$ (N1)	8	$2a_1, 2a_2, 2a_3$	$(Aa_{1/16})^{16}(B^a_{1/16})^{32}(X^a_{1/16})^{64}$

where the main diagonal is written in a column;  $h_i$  is a rotation part of the symmetry element  $g_i = \{h_i | \tau_i\}$  of the  $Fd\bar{3}m$  group,  $\tau_i$  is the accompanying nontrivial translation of  $h_i$ , and  $a_1, a_2, a_3$  are basic vectors of the primitive cell. In eqn (1) the generators of irrep  $\mathbf{k}_9(\tau_4)$  of  $Fd\bar{3}m$  group symmetry are given. The remaining irrep  $\mathbf{k}_9(\tau_4)$  matrices corresponding to other elements of  $Fd\bar{3}m$  group symmetry can be obtained as a result of multiplication of the above-mentioned matrices. Designations for symmetry elements of the  $Fd\bar{3}m$  space group are given according to Kovalev.<sup>33</sup>

Table 2 lists the space groups of all possible low-symmetry phases induced by irrep  $\mathbf{k}_9(\tau_4)$ , and corresponding components of the four-dimensional OP. The multiplication of primitive cell volumes as a result of the structural phase transitions ( $V_0/V$ ), the vectors of primitive cell translations of low-symmetry phases ( $a_1, a_2, a_3$ ) and the structure formulas of low-symmetry phases are also presented. All these types of solutions are necessary for constructing possible phase diagrams, for establishing the thermodynamic nature of the phase transition under study, and for predicting new possible phase states in  $CuTi_2S_4$  and structurally related materials. The list of low-symmetry phases (Table 2) is consistent with the results obtained in ref. 34.

It is interesting to note that among the 11 low-symmetrical phases, there are two one-parameter phases with the same space group  $R\bar{3}m$ . However, the structures of these isosymmetrical phases differ significantly.

## 2.2. Phase diagram

The basis of invariants of the thermodynamic potential consists of 43 monomials that do not exceed the eighth degree:

$$J_1 = \eta_1^2 + \eta_2^2 + \eta_3^2 + \eta_4^2,$$

$$J_2 = \eta_1^2\eta_2^2 + \eta_1^2\eta_3^2 + \eta_1^2\eta_4^2 + \eta_2^2\eta_3^2 + \eta_2^2\eta_4^2 + \eta_3^2\eta_4^2,$$

$$J_3 = \eta_1^2\eta_2^2\eta_3^2 + \eta_1^2\eta_2^2\eta_4^2 + \eta_1^2\eta_3^2\eta_4^2 + \eta_2^2\eta_3^2\eta_4^2,$$

$$J_4 = \eta_1^2\eta_2^2\eta_3^2\eta_4^2 \quad (2)$$

The invariant basis (2) was constructed using the algorithm described in ref. 35. A phenomenological thermodynamic model of phase transitions will be built taking into account the thermodynamic potential stability.<sup>36–39</sup> The term “stable” refers

to the potential that allows us to construct a phase diagram that does not change due to a small external perturbation to the potential. A small perturbation should lead to only small quantitative changes without changing the type, the number of phases and the topology of the phase diagrams.

To build a “stable” thermodynamic potential the type of multi-critical point should be specified.<sup>37</sup> The “stable” thermodynamic potential of the sixth degree is only possible if the critical point is determined by the lack of invariants  $J_1$  and  $J_1^2$ . A stable potential has the form:

$$F = a_1J_1 + a_2J_1^2 + b_2J_2 + a_3J_1^3 + b_{12}J_1J_2 + c_3J_3 \quad (3)$$

Potential (3) at  $b_2 > 0$  and  $b_{12} > 0$  on plane ( $a_1, a_2$ ) describes a phase transition into the  $R\bar{3}m$ -phase.

As in thermodynamic potential (3) there is no invariant of the third degree on components of the OP, any phenomenological model of a phase transition with the OP which has symmetry (1) will describe only phase transitions of the second order between the high-symmetry phase and low-symmetry phases bordering it.

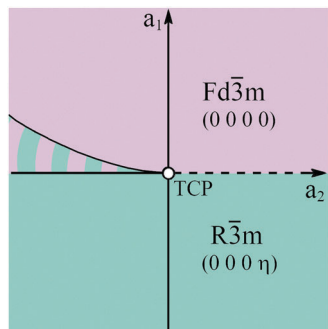
The point  $a_1 = a_2 = 0$  in the phase diagram (Fig. 1) is a tricritical point (TCP). At this point, the line of phase transitions of the second order continuously passes through the line of phase transitions of the first order. It is important to emphasize that the first order of the phase transition from the  $Fd\bar{3}m$ -phase to the  $R\bar{3}m$ -phase at  $a_2 < 0$  is caused by the sixth degree of order parameter components but not by the symmetry of the system. The irreversibility of the phase transition in  $CuTi_2S_4$  established experimentally<sup>18</sup> indicates that in this substance there is a phase transition  $Fd\bar{3}m \rightarrow R\bar{3}m$  of the first order in the vicinity of the TCP in the region of the phase diagram  $a_2 < 0$ .

## 2.3. Structural mechanism of rhombohedral modification formation

The structural mechanism of formation of low-symmetry modifications of crystals is determined by the ordering of atoms and their displacements in the initial phase structure.

The Cu-atoms occupy Wyckoff position 8a (site symmetry  $\bar{3}m$ ), Ti – Wyckoff position 16d (site symmetry  $\bar{4}3m$ ), sulfur – Wyckoff position 32e (site symmetry  $3m$ ) in the cubic  $Fd\bar{3}m$ -phase of a





**Fig. 1** Phase diagram described by thermodynamic potential (3). The diagram in the vicinity of the tricritical point (TCP) for the case where  $b_2 > 0$  and  $b_{12} > 0$ . The lines of the first- and second-order transitions are indicated by solid and dashed lines, respectively. The region of the phase diagram decorated with two colors is the two-phase region.

normal spinel. The structural formula of the cubic  $Fd\bar{3}m$ -spinel is  $(\text{Cu})^{8a}[\text{Ti}_2]^{16d}\text{S}_4^{32e}$ .

The critical irrep  $\mathbf{k}_9(\tau_4)$  enters into the mechanical representation and permutation representation of the spinel structure on Wyckoff positions 8a, 16d and 32e.<sup>21–24,27</sup> This means that the low-symmetry phase formation is connected with displacements of tetrahedral and octahedral cations and anions and also with the ordering of all atom types. Group-theoretic analysis showed that the formation of the  $\text{CuTi}_2\text{S}_4$  rhombohedral phase is accompanied by the following types of atom ordering:

- binary tetrahedral cation ordering (order type 1 : 1);
- ternary octahedral cation ordering (order type 1 : 1 : 6);
- quaternary anion ordering (order type 1 : 1 : 3 : 3).

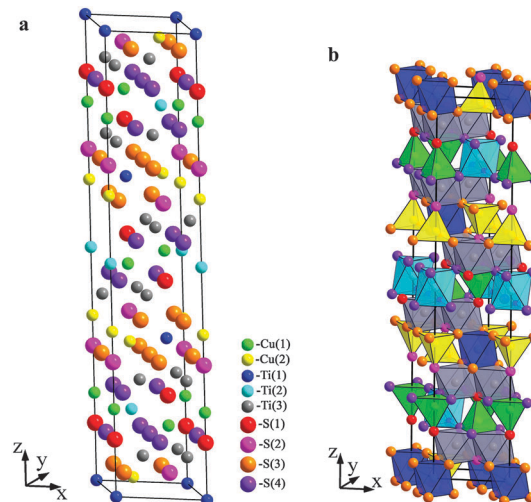
As a result, the theoretical structure formula of a low-symmetry rhombohedral  $R\bar{3}m$ -spinel modification should be  $A^{2c}_{1/2}A^{2c}_{1/2-}B^{1a}_{1/4}B^{1b}_{1/4}B^{6h}_{3/2}X^{2c}_{1/2}X^{2c}_{1/2}X^{6h}_{3/2}X^{6h}_{3/2}$  (rhombohedral presentation) or  $A^{6c}_{1/2}A^{6c}_{1/2}B^{3a}_{1/4}B^{3b}_{1/4}B^{18h}_{3/2}X^{6c}_{1/2}X^{6c}_{1/2}X^{18h}_{3/2}X^{18h}_{3/2}$  (hexahedral presentation). For  $\text{CuTi}_2\text{S}_4$  the latest structural formula is  $\text{Cu}(1)^{6c}_{1/2}\text{Cu}(2)^{6c}_{1/2}\text{Ti}(1)^{3a}_{1/4}\text{Ti}(2)^{3b}_{1/4}\text{Ti}(3)^{18h}_{3/2}\text{S}(1)^{6c}_{1/2-}\text{S}(2)^{6c}_{1/2}\text{S}(3)^{18h}_{3/2}\text{S}(4)^{18h}_{3/2}$ . Our theoretical structural formula agrees with experimental data.<sup>18</sup>

Note that the  $\text{CuTi}_2\text{S}_4$  compound under consideration can have charge ordering in principle, because copper and titanium atoms, being in Wyckoff positions 8a and 16d of the spinel structure, occupy some different Wyckoff positions in rhombohedral spinel modification.

We have built the scalar and vector basic functions of irrep  $\mathbf{k}_9(\tau_4)$  which allowed us to deduce the rhombohedral  $R\bar{3}m$ -spinel structure from the spinel structure. We used the value of the free parameters for Wyckoff positions of atoms in rhombohedral spinel modification (which were taken from ref. 18) in order to build the  $R\bar{3}m$ -spinel structure. The results of theoretical calculations of the  $\text{CuTi}_2\text{S}_4$  atom structure are given below (Fig. 2).

#### 2.4. Metal clusters in the structure of $\text{CuTi}_2\text{S}_4$

There are two independent Wyckoff positions for Cu, three for Ti (two Ti atoms are located in the triangular lattice [Ti(1) and Ti(2)], and one Ti atom [Ti(3)] is in the kagome lattice), and four for S in the rhombohedral  $R\bar{3}m$ -spinel structure of the title



**Fig. 2** Calculated low-symmetry ordered  $R\bar{3}m$ -spinel structure: atomic presentation (a), polyhedral presentation in the form of  $\text{Cu}(2)[\text{S}(3)_3\text{S}(2)]$  (yellow) and  $\text{Cu}(1)[\text{S}(4)_3\text{S}(1)]$  (green) tetrahedra and  $\text{Ti}(1)[\text{S}(3)_6]$  (dark blue),  $\text{Ti}(2)[\text{S}(4)_6]$  (blue) and  $\text{Ti}(3)[\text{S}(1)\text{S}(2)\text{S}(3)_2\text{S}(4)_2]$  (gray) octahedra (b).

compound (Fig. 2). This compound is isostructural with  $\text{CuZr}_{1.86(1)}\text{S}_4$ ,<sup>40</sup> with rhombohedral modification of  $\text{AlV}_2\text{O}_4$ <sup>20</sup> and with phase of high pressure of  $\text{LiV}_2\text{O}_4$ .<sup>41</sup>

A peculiar feature of the rhombohedral structure is metal clustering.

In contrast to the  $\text{AlV}_2\text{O}_4$  rhombohedral structure, in which the formation of heptamers occurs by the ordering of vanadium atoms, located in octahedral sites of the initial cubic spinel, in the formation of metal clusters in the  $\text{CuTi}_2\text{S}_4$  rhombohedral structure not only the octahedral titanium atoms but also tetrahedral atoms of copper take part (Fig. 3).

Atoms of Cu(1) and Ti(3) form a “bunch” of dimers (Fig. 3 and 4). Each “bunch” consists of three [Cu(1)–Ti(3)]-dimers which are joined by the common Cu(1)-atom. Each Cu(1) atom is surrounded by three Ti(3) atoms, resulting in three Cu(1)–Ti(3) interatomic distances of 2.876 Å. The shortest Cu–Ti distance in the cubic spinel is much longer and equal to 4.148 Å. This distance is too large for a significant interaction, while it is the shortest among all the bond lengths of the metal–metal bonds in the rhombohedral form.

On the kagome lattice, there are two kinds of Ti(3)–Ti(3) bonds (titanium dimers [Ti(3)<sub>2</sub>]) with different bond lengths: the shorter (dark blue) is 3.419 Å and the longer (red) is 3.606 Å (Fig. 5a and b). These dimers alternate in the kagome lattice (Fig. 5a). The distance Ti–Ti in the cubic form of  $\text{CuTi}_2\text{S}_4$  is equal to 3.538 Å.

Ti(3)-atoms, belonging to the “bunch”, form two types of [Ti(3)<sub>3</sub>] trimers with interatomic distances Ti(3)–Ti(3) = 3.419 Å (Fig. 5a) and Ti(3)–Ti(3) = 3.606 Å (Fig. 3 and 5b).

Alternating trimers, having short and long bonds Ti(3)–Ti(3), form a kagome lattice (Fig. 5a). These trimers are at the basis of two types of tetrahedra: [Cu(1)Ti(3)<sub>3</sub>] and [Ti(1)Ti(3)<sub>3</sub>]. They have the opposite orientation (antiparallel) relative to the kagome-plane (Fig. 5b).

Each trimer, formed by bonds Ti(3)–Ti(3), is the basis for the metal tetrahedron with the shortest bonds: [Cu(1)Ti(3)<sub>3</sub>] and [S(2)Cu(2)Ti(3)<sub>3</sub>] (Fig. 5c). Each trimer, formed by more longer



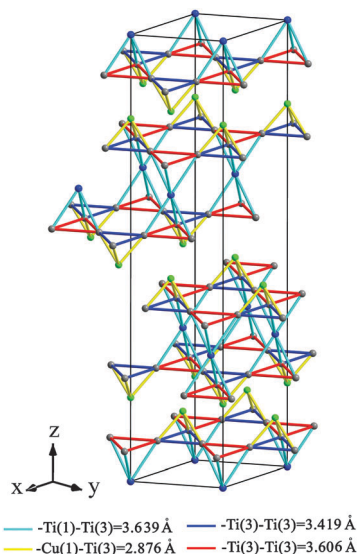


Fig. 3 The Cu- and Ti-ions in the low-symmetry ordered phase of  $\text{CuTi}_2\text{S}_4$ . There are three inequivalent Ti ions (Ti(1), Ti(2), Ti(3)). The Ti–Ti bond lengths are substantially different (they are marked by different colors).

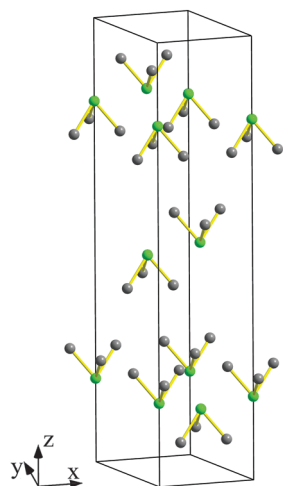


Fig. 4 "Bunch" of [Cu(1)–Ti(3)]-dimers.

bonds Ti(3)–Ti(3), is the basis for the metal tetrahedron  $[\text{Ti}(1)\text{Ti}(3)_3]$ . Each  $[\text{Cu}(1)\text{Ti}(3)_3]$ -tetrahedron through the Cu(1)-atom is surrounded by three S(1)-atoms and by  $[\text{S}(1)\text{Cu}(1)\text{Ti}(3)_3]$ -tetrahedron (Fig. 5c).

In the rhombohedral structure of  $\text{CuTi}_2\text{S}_4$  it is possible to distinguish Ti(1)-heptamers, which are analogs of V-heptamers in the structure of  $\text{AlV}_2\text{O}_4$ <sup>19</sup> (Fig. 6a). Indeed, there are two inequivalent triangular-lattice layers, composed of Ti(1)-atoms and Ti(2)-atoms, respectively. Here, all the Ti(1) atoms are sandwiched by two  $[\text{Ti}(3)_3]$ -trimers (Fig. 6a), but none of the Ti(2) atoms are. Ti(2)-atoms are sandwiched by two  $[\text{S}(4)_3]$ -trimers and S(4) atoms also constitute also one heptamer  $[\text{Ti}(2)\text{S}(4)_6]$  (Fig. 6b). But these S(4)-heptamers are not analogs of V-heptamers in the structure of  $\text{AlV}_2\text{O}_4$ .

Binding between adjacent kagome-layers is carried out by using heptamers  $[\text{Ti}(1)\text{Ti}(3)_6]$  (Fig. 6a, c and d) and sulfur atoms (Fig. 6c and d).

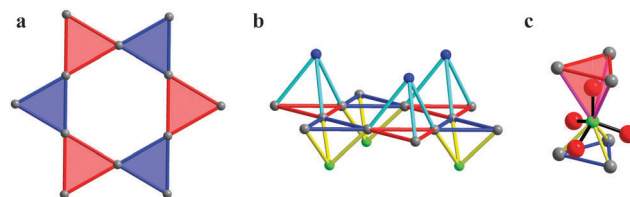


Fig. 5 Two types of  $[\text{Ti}(3)_2]$ -dimers (dark blue and red) and  $[\text{Ti}(3)_3]$ -trimers (dark blue and red) (a),  $[\text{Cu}(1)\text{Ti}(3)_3]$ - and  $[\text{Ti}(1)\text{Ti}(3)_3]$ -tetrahedra clusters (b), nearest neighbors of the Cu(1)-atom (c).

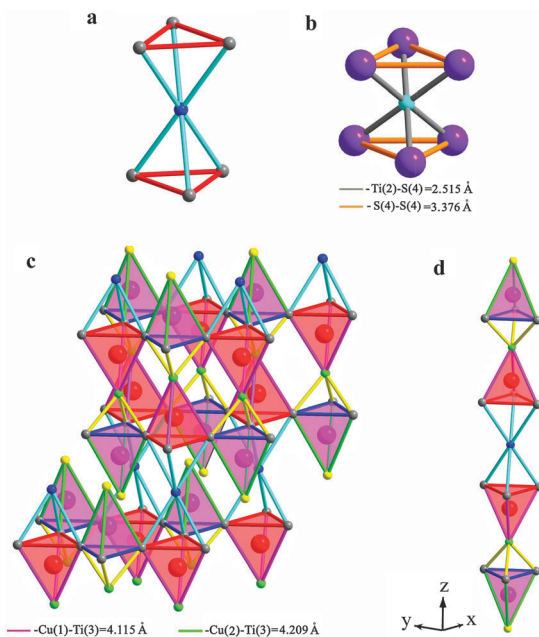


Fig. 6  $[\text{Ti}(1)\text{Ti}(3)_6]$ - and  $[\text{Ti}(2)\text{S}(4)_6]$ -heptamers in the  $\text{CuTi}_2\text{S}_4$  rhombohedral structure.  $[\text{Ti}(1)\text{Ti}(3)_6]$ -heptamers, each of which is made of one Ti(1) (dark blue) and six Ti(3) ions (grey) connected by the shorter Ti–Ti bonds (shown by red), can be seen.  $[\text{Ti}(1)\text{Ti}(3)_6]$  heptamers (a),  $[\text{Ti}(2)\text{S}(4)_6]$ -heptamers (b), heptamers located between kagome-layers (c), and the entourage of  $[\text{Ti}(1)\text{Ti}(3)_6]$  heptamers in the direction  $[111]$  (d). Tetrahedra  $[\text{S}(1)\text{Cu}(1)\text{Ti}(3)_3]$  are shown in red.

Previously, the authors<sup>18</sup> suggested that the valence states of atoms in the  $\text{CuTi}_2\text{S}_4$  rhombohedral form should be  $(\text{Cu}^+)_4\text{Ti}(1)^{4+}\text{Ti}(2)^{3+}\text{Ti}(3)_6^{3.5+}(\text{S}^{2-})_{16}$  according to the crystal-chemical analysis of the crystal bond lengths and electronic structure calculations. This formula means that the  $\text{Ti}(1)^{4+}$  ion has no  $t_{2g}$  orbitals, *i.e.* there are no chemical bonding between Ti(1) and Ti(3) atoms. Therefore, the formation of Ti-heptamers is unlikely. Besides, the calculated densities of states of rhombohedral modifications show that Cu(1)–Ti(3) and Ti(3)–Ti(3) interactions in the "bunch" of dimers and  $[\text{Ti}(3)_3]$  trimers (with interatomic distances Ti(3)–Ti(3) = 3.419 Å) have a bonding character.<sup>18</sup>

### 3. Results and discussion

For the first time we investigated the OP symmetry, thermodynamics, and structural mechanism of formation of the low-symmetry  $\text{CuTi}_2\text{S}_4$  phase within a unified approach based on the Landau phenomenological theory of phase transitions.



Based on the hypothesis of one critical representation, we calculated stratification of the Wyckoff positions 8a, 16d, and 32e of the initial phase with a cubic spinel structure upon transition to the low-symmetry rhombohedral modification. We also showed that the calculated structure of the  $\text{CuTi}_2\text{S}_4$  rhombohedral phase is formed due to displacements of all types of atoms and the ordering of Cu-atoms (1:1 order type in tetrahedral spinel sites), Ti-atoms (1:1:6 order type in octahedral spinel sites), and S-atoms (1:1:3:3 order type).

Crystallochemical features of the structure of the ordered rhombohedral modification were investigated theoretically, and the structural motifs of atomic and polyhedral short- and long-range orders were found. Our theoretical structural results agree well with the experimental data.<sup>18</sup> We found that in the  $\text{CuTi}_2\text{S}_4$  rhombohedral structure there are only one type of Ti-heptamers such as V-heptamers in  $\text{AlV}_2\text{O}_4$ .<sup>20</sup> But these heptamers have very large bond lengths and therefore cannot be considered as metal “molecules” in the  $\text{CuTi}_2\text{S}_4$  rhombohedral structure.

We first established the existence of a “bunch” of  $[\text{Cu}(1)\text{-Ti}(3)]$ -dimers, two types of  $\text{Ti}(3)$ -trimers  $[\text{Ti}(3)_3]$  and two types tetrahedral clusters  $[\text{Cu}(1)\text{Ti}(3)_3]$  and  $[\text{Ti}(1)\text{Ti}(3)_3]$ . Of particular interest are metal nanostructures:  $[\text{Cu}(1)\text{-Ti}(3)]$ -dimers,  $[\text{Ti}(3)_3]$  trimers with the shorter bond lengths and a “bunch” of  $[\text{Cu}(1)\text{-Ti}(3)]$ -dimers. The metallic dimers and trimers in geometrically frustrated structures (for example dimers:  $\text{MgTi}_2\text{O}_4$ ,<sup>43–45</sup>  $\text{CuTe}_2\text{O}_5$ ,<sup>46,47</sup>  $\text{VO}_2$ ,<sup>48</sup>  $\text{CuGeO}_3$ ;<sup>49</sup> trimers:  $\text{LiVO}_2$ ,<sup>50</sup>  $\text{LiVS}_2$ ,<sup>51</sup>  $\text{NaV}_6\text{O}_{10}$ ,<sup>52</sup>  $\text{BaV}_{10}\text{O}_{15}$ ,<sup>53–56</sup>  $\text{SrV}_8\text{Ga}_4\text{O}_{19}$ ,<sup>57</sup>  $\text{AV}_{13}\text{O}_{18}$  (A = Ba, Sr),<sup>58</sup>  $\text{A}_2\text{V}_{13}\text{O}_{22}$  (A = Ba, Sr),<sup>59</sup>  $\text{Ba}_4\text{Ru}_3\text{O}_{10}$ <sup>60</sup>) have long been known. The formation of a “bunch” of  $[\text{Cu}(1)\text{-Ti}(3)]$ -dimers, which are molecular-like clusters (metal “molecules”), in  $\text{CuTi}_2\text{S}_4$  can be regarded as a new type of self-organization of atoms in the crystals.

The global pattern of changes in the phase states was considered within the model taking into account the terms in the free energy up to the sixth degree in the OP components in the Landau theory of phase transitions. It was shown first that phase transitions between different phases ( $Fd\bar{3}m$  and  $R\bar{3}m$ ) may occur as a result of both second and first-order phase transitions in the vicinity of the tricritical point. In the case of  $\text{CuTi}_2\text{S}_4$ , we propose that phase transitions of the first order close to the second order in the vicinity of the TCP take place. 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.<sup>42</sup> These results are based on our calculations of the phase diagram and the experimental fact of irreversibility of the phase transition.<sup>18</sup>

It is interesting to note that the magnetization of some spinels normally takes place along the  $[111]$  direction and therefore could be responsible for a rhombohedral distortion. But, magnetic interactions are not the driving force for the phase transformation of the “cubic-rhombohedral” spinel in the  $\text{CuTi}_2\text{S}_4$  case as both phases are Pauli paramagnets.<sup>18</sup> The Pauli susceptibility of the  $R\bar{3}m$  form is larger than that of the thiospinel in quantitative agreement with the LMTO-ASA band structure calculations.<sup>18</sup> The authors<sup>18</sup> point out that a transition

to the ferromagnetic state might occur below the temperature range investigated (2–300 K). The magnetic structure of  $\text{CuTi}_2\text{S}_4$  near 2 K remains unknown.

## 4. Conclusions

We first proposed a theory of the structural phase transition in  $\text{CuTi}_2\text{S}_4$ , built possible phase diagrams and established a structural mechanism of formation of the low-symmetry rhombohedral modification from the high-symmetry cubic spinel phase. The most important and unexpected result is the discovery of metal nanoclusters, which are different from the V-heptamers in the  $\text{AlV}_2\text{O}_4$  structure.

We believe that further studies will be connected with specifying the conditions for stability of metallic nanoclusters. For this it is necessary to perform detailed quantum mechanical calculations of the Cu and Ti valence states as well as the calculations of the spin and orbital ordering in the rhombohedral phase of  $\text{CuTi}_2\text{S}_4$ .

## Acknowledgements

The authors thank the anonymous referees for valuable remarks. They are also very grateful to Professor Dr Katsuhiko Ariga for his kind interest and encouragement. The reported study was funded by RFBR, according to research project no. 16-32-60025 mol\_a\_dk (Talanov M. V.).

## References

- 1 R. P. Van Stapele, *Ferro-magnetic Materials, A Handbook on the properties of magnetically ordered Substances*, Amsterdam, North-Holland, 1982, vol. 3.
- 2 F. Hulliger, *Structure and Bonding V.4.*, Springer, Berlin, Crystal Chemistry of the Chalcogenides and Pnictides of the Transition Elements, 1968, p. 83.
- 3 V. M. Talanov, *Energetic Crystallochemistry of Multisublattice Crystals*, Rostov-on-Don, RSU, 1986.
- 4 T. Furubayashi, H. Suzuki, N. Kobayashi and S. Nagata, *Solid State Commun.*, 2004, **131**, 505.
- 5 T. Bitoh, T. Hgino, Y. Seki, S. Chikazawa and S. Nagata, *J. Phys. Soc. Jpn.*, 1992, **61**, 3011.
- 6 T. Hagino, Y. Seki, N. Wada, S. Tsuji, T. Shirane, K. I. Kumagai and S. Nagata, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1995, **51**, 12673.
- 7 N. H. Van Maaren, G. M. Schaeffer and F. K. Lotgering, *Phys. Lett.*, 1967, **25**, 238.
- 8 R. N. Shelton, D. C. Jhonston and H. Adrian, *Solid State Commun.*, 1976, **20**, 1077.
- 9 T. Shirane, T. Hgino, Y. Seki, S. Chikazawa and S. Nagata, *J. Phys. Soc. Jpn.*, 1993, **62**, 374.
- 10 M. Ito, J. Hori, H. Kurisaki, H. Okada, A. J. Perez Kuroki, N. Ogita, M. Udagawa, H. Fujii, F. Nakamura, T. Fijita and T. Suzuki, *Phys. Rev. Lett.*, 2003, **91**, 077001.
- 11 S. Nagata, T. Hagino, Y. Seki and T. Bitoh, *Physica B*, 1995, **194–196**, 12673.



- 12 P. G. Radaelli, Y. Horibe, M. J. Gutmann, H. Ishibashi, C. H. Chen, R. M. Ibberson, Y. Koyama, Y.-S. Hor, V. Kiryukhin and S.-W. Cheong, *Nature*, 2002, **416**, 155.
- 13 T. Furubayashi, T. Matsumoto, T. Hagino and S. Nagata, *J. Phys. Soc. Jpn.*, 1994, **63**, 3333.
- 14 N. Matsumoto, T. Hagino, K. Taniguchi, S. Chikazawa and S. Nagata, *Physica B*, 2000, **284–288**, 1978.
- 15 T. Koyama, H. Sugita, S. Wada, K. Miyatani, T. Tanaka and M. Ishikawa, *Physica B*, 2000, **284–288**, 1513.
- 16 M. Isoda and S. Mori, *J. Phys. Soc. Jpn.*, 2000, **69**, 1509.
- 17 H. Okada, K. Koyama, K. Watanabe and J. Alloys, *Compounds*, 2005, **403**, 34.
- 18 N. Soheilnia, K. M. Kleinke, E. Dashjav, H. L. Cuthbert, J. E. Greedan and H. Kleinke, *Inorg. Chem.*, 2004, **43**, 6473.
- 19 Y. Horibe, M. Shingu, K. Kurushima, H. Ishibashi, N. Ikeda, K. Kato, Y. Motome, N. Furukawa, S. Mori and T. Katsufuji, *Phys. Rev. Lett.*, 2006, **96**, 086406.
- 20 M. Croft, V. Kiryukhin, Y. Horibe and S.-W. Cheong, *New J. Phys.*, 2007, **9**, 1.
- 21 V. M. Talanov and V. B. Shirokov, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2012, **68**, 595.
- 22 V. M. Talanov and V. B. Shirokov, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2014, **70**, 49.
- 23 V. M. Talanov, V. B. Shirokov and M. V. Talanov, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2015, **71**, 301.
- 24 V. M. Talanov, M. V. Talanov and V. B. Shirokov, *Crystallogr. Rep.*, 2014, **59**, 650.
- 25 V. M. Talanov and A. A. Mukovnin, *Eur. Phys. J. B*, 2013, **86**, 448.
- 26 A. A. Mukovnin and V. M. Talanov, *Eur. Phys. J. B*, 2014, **87**, 34.
- 27 V. P. Sahnenko, V. M. Talanov and G. M. Chechin, *Fiz. Met. Metalloved.*, 1986, **62**, 847.
- 28 V. M. Talanov and V. B. Shirokov, *Kristallografiya*, 2013, **58**, 296.
- 29 V. M. Talanov and V. B. Shirokov, *Crystallogr. Rep.*, 2013, **58**, 314.
- 30 H. T. Stokes and D. M. Hatch, 2007, ISOTROPY, <http://stokes.byu.edu/iso/isotropy.html>.
- 31 H. T. Stokes, E. H. Kisi, D. M. Hatch and C. J. Howard, *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.*, 2002, **58**, 934.
- 32 L. D. Landau and E. M. Lifshitz, *Statistical Physics, Part 1*, Oxford, Pergamon, 1980.
- 33 O. V. Kovalev, in *Representations of Crystallographic Space Groups. Irreducible Representations, Induced Representations and Co-representations*, ed. H. T. Stokes and D. M. Hatch, Taylor and Francis Ltd, London, 1992, p. 349.
- 34 V. P. Sahnenko, V. M. Talanov and G. M. Chechin, Tomsk, Dep. VINITI No. 638-82, 1982, 25.
- 35 V. B. Shirokov, *Crystallogr. Rep.*, 2011, **56**, 475.
- 36 A. M. Prokhorov, Yu. M. Gufan, E. S. Larin, E. G. Rudashevsky and V. B. Shirokov, *DAN SSSR*, 1984, **227**, 1369.
- 37 E. I. Kut'in, V. L. Lorman and S. V. Pavlov, *Usp. Fiz. Nauk*, 1991, **34**, 497.
- 38 T. Poston and I. Stewart, *Catastrophe Theory and its Applications*, Pitman, London-San Francisco-Melbourne, 1978.
- 39 V. I. Arnold, *Catastrophe Theory*, Springer-Verlag, Berlin, 3rd edn, 1992.
- 40 Y. Dong, M. A. McGuire, H. Yun and F. J. DiSalvo, *J. Solid State Chem.*, 2010, **183**, 606.
- 41 K. Takeda, H. Hidaka, H. Kotegawa, T. C. Kobayashi, K. Shimizu, H. Harima, K. Fujiwara, K. Miyoshi, J. Takeuchi, Y. Ohishi, T. Adachi, M. Takata, E. Nishibori, M. Sakata, T. Watanuki and O. Shimomura, *Physica B*, 2005, **359–361**, 1312.
- 42 Yu. M. Gufan, *Structural Phase Transitions*, Nauka, Moscow, 1982, p. 304.
- 43 M. Schmidt, W. Ratcliff, P. G. Radaelli, K. Refson, N. M. Harrison and S.-W. Cheong, *Phys. Rev. Lett.*, 2004, **92**, 056402.
- 44 V. M. Talanov, V. B. Shirokov, V. V. Ivanov and M. V. Talanov, *Crystallogr. Rep.*, 2015, **60**(1), 101.
- 45 V. V. Ivanov, V. M. Talanov, V. B. Shirokov and M. V. Talanov, *Inorg. Mater.*, 2011, **47**(9), 990.
- 46 K. Hanke, V. Kupcik and O. Lindqvist, *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.*, 1973, **29**, 963.
- 47 A. V. Ushakov and S. V. Streltsov, *J. Phys.: Condens. Matter*, 2009, **21**, 305501.
- 48 M. Imada, A. Fujimori and Y. Tokura, *Rev. Mod. Phys.*, 1998, **70**, 1039.
- 49 M. Hase, I. Terasaki and K. Uchinokura, *Phys. Rev. Lett.*, 1998, **70**, 3651.
- 50 H. F. Pen, L. H. Tjeng, E. Pellegrin, F. M. F. de Groot, G. A. Sawatzky, M. A. van Veenendaal and C. T. Chen, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1997, **55**, 15500.
- 51 N. Katayama, M. Uchida, D. Hashizume, S. Niitaka, J. Matsuno, D. Matsumura, Y. Nishihata, J. Mizuki, N. Takeshita, A. Gauzzi, M. Nohara and H. Takagi, *Phys. Rev. Lett.*, 2009, **103**, 146405.
- 52 H. Kato, M. Kato, K. Yoshimura and K. Kosuge, *J. Phys. Soc. Jpn.*, 2001, **70**, 1404.
- 53 G. Liu and J. E. Greedan, *J. Solid State Chem.*, 1996, **122**, 416.
- 54 C. A. Bridges, J. E. Greedan and H. Kleinke, *J. Solid State Chem.*, 2004, **177**, 4516.
- 55 A. Bridges and J. E. Greedan, *J. Solid State Chem.*, 2004, **177**, 1098.
- 56 T. Kajita, T. Kanzaki, T. Suzuki, J. E. Kim, K. Kato, M. Takata and T. Katsufuji, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **81**, 060405.
- 57 J. Miyazaki, T. Sonehara, D. Akahoshi, H. Kuwahara, J. E. Kim, K. Kato, M. Takata and T. Katsufuji, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2009, **79**, 180410(R).
- 58 M. Ikeda, T. Okuda, K. Kato, M. Takata and T. Katsufuji, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **83**, 134417.
- 59 J. Miyazaki, K. Matsudaira, Y. Shimizu, M. Itoh, Y. Nagamine, S. Mori, J. E. Kim, K. Kato, M. Takata and T. Katsufuji, *Phys. Rev. Lett.*, 2010, **104**, 207201.
- 60 S. V. Streltsov and D. I. Khomskii, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, **86**, 064429.

