

## Multi-order and structural mechanism of atom nanocluster formation in rhombohedral Cu–Zr-thiospinels

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**ABSTRACT** A structural mechanism for the formation of nanoclusters and the rhombohedral modification of  $\text{CuZr}_{1.86(1)}\text{S}_4$  has been proposed. Group-theoretical and crystal-chemical methods are used to study the features of the crystal structure and multi-order in Cu–Zr-thiospinel. A multi-order is a structural organization of a material, in the formation of which different degrees of freedom of a crystal participate. It has been proven that the rhombohedral structure of  $\text{CuZr}_{1.86(1)}\text{S}_4$  is formed as a result of displacements and orderings of all types of atoms. It is theoretically shown that the formation of a rhombohedral phase is associated not only with the lattice, but also with the charge and, possibly, orbital degrees of freedom of the crystal. Theory predicts that the rhombohedral phase must be an improper ferroelastic. An important feature of the rhombohedral structure is metal nanoclusters: “bunch” of dimers, trimers, and tetrahedra. Bunch of dimers are an unusual type of self-organization of atoms in rhombohedral spinel-like structures, formed by atoms of two (tetrahedral and octahedral) frustrated crystal sublattices.

**KEYWORDS** order parameter, multi-order, structural mechanism, rhombohedral modification, nanocluster

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### 1. Introduction

Copper thiospinels with a chemical formula  $\text{CuB}_2\text{S}_4$  (where B is a transition metal) attract much attention because of wide variety of the physical properties. These are superconductivity ( $\text{CuRh}_2\text{S}_4$  [1, 2],  $\text{Cu}_{1-x}\text{Zn}_x\text{Ir}_2\text{S}_4$ ,  $0.25 \leq x \leq 0.8$  [3–5]), pressure-induced superconductor-insulator transition in  $\text{CuRh}_2\text{S}_4$  [6], charge ordering and charge-density waves in  $\text{CuV}_2\text{S}_4$  [7,8], exotic types of orbital ordering (orbital octamers in  $\text{CuIr}_2\text{S}_4$  [9]), large negative magnetoresistance in  $\text{CuCrZrS}_4$  [10], unusual short-range magnetic ordering in  $\text{Cu}_{1/2}\text{In}_{1/2}\text{Cr}_2\text{S}_4$  [11], quantum spin liquid and/or heavy fermion-like states (as assumed in  $\text{CuTi}_2\text{S}_4$  [12]). In many cases, the unique properties are related to a specific structural feature of  $\text{AB}_2\text{X}_4$  spinels: the presence of a three-dimensional network of tetrahedra  $(\text{B}_4)_\infty$  (the so-called pyrochlore sublattice) formed by octahedral B cations (Fig. 1). Such a lattice is an integral part of many crystals belonging to various structural types (pyrochlores, spinels, Laves phases (C15), compounds of the  $\beta$ -alumina family and others). Anderson proved that the pyrochlore lattice causes strong geometrical frustration effects, which are responsible for the unusual physical properties of the crystals [13]. Geometric frustration causes the degeneracy of the ground state of the crystals, which leads to the fact that even a slight external perturbation can affect the properties of matter and, in particular, lead to the formation of exotic phases with unusual properties, nontrivial atomic, charge and orbital ordering. One of the degeneracy removal mechanisms is the formation of metal clusters, called “orbital molecules”, in the form trimers in  $\text{Fe}_3\text{O}_4$  [14], octamers in  $\text{CuIr}_2\text{S}_4$  [9, 15], dimers in  $\text{MgTi}_2\text{O}_4$  [16–18], and metal clusters in many other substances [19–22].

In our previous works [21,23,24], we studied the structural mechanisms of the formation of “orbital molecules” in the crystals using crystal chemical and group-theoretical approaches and showed the involvement of different degrees of freedom (lattice, spins, orbitals, and charges) in the formation of these “molecules”. The emergence of a complex multi-order state is expected in the rhombohedrally distorted spinels with the  $R\bar{3}m$  space group [25,26]. In addition, it is important to note that the  $\text{CuZr}_2\text{O}_4$  compound is a structural analogue of  $\text{CuTi}_2\text{S}_4$  and crystallizes in the spinel type of structure [27]. When  $\text{CuTi}_2\text{S}_4$  prepared in a flux at low temperatures, the rhombohedral form is obtained. In the cubic form the Cu–Ti distances are too large for a significant interaction, while in the rhombohedral form that distance is much shorter and perhaps this interaction plays a role in the stabilization of the rhombohedral phase [28]. The rhombohedral phase of  $\text{CuTi}_2\text{S}_4$

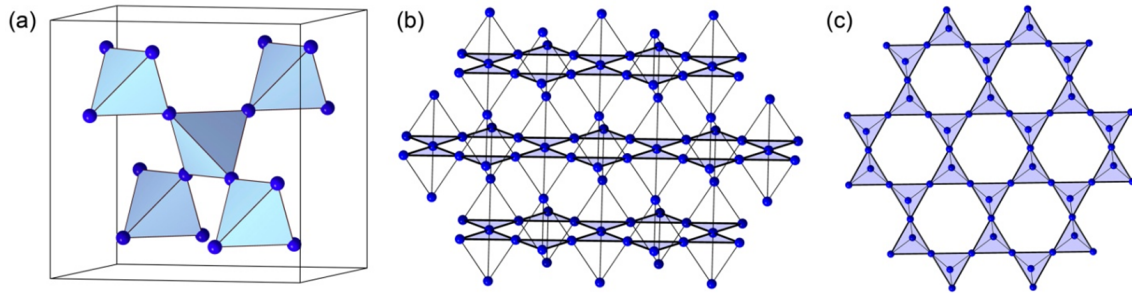


FIG. 1. The pyrochlore B-sublattice of spinels. A three dimensional network of tetrahedra (a), B-spinel sublattice as a stacking of kagome layers (b), view of a plane perpendicular to the [111]-type direction in the spinel (c).

contains various metal clusters [25]. Therefore, we can expect the existence of similar clusters in the rhombohedral phase of  $\text{CuZr}_2\text{O}_4$ . However, the rhombohedral phase in Cu–Zr-thiospinel is obtained only at a nonstoichiometric composition  $\text{CuZr}_{1.86(1)}\text{S}_4$ , in which, as can be assumed by analogy with  $\text{CuTi}_2\text{S}_4$ , Cu–Zr interactions stabilize the existence of a rhombohedral phase with a deficit of zirconium atoms and, consequently, the formation clusters.

In this work, we consider a multi-order and structural mechanism of the formation of metal nanoclusters in known rhombohedral nonstoichiometric thiospinel  $\text{CuZr}_{1.86(1)}\text{S}_4$ .

## 2. Critical and noncritical order parameters

Cubic spinel phase of  $\text{CuZr}_2\text{S}_4$  crystallizes in the  $Fd\bar{3}m$  space group with the unit cell dimension  $a_c = 10.378(3)$  Å (anions located in Wyckoff position  $32e$  with “adjusted” parameter  $x$  equal 0.375) [27]. The rhombohedral modification of the thiospinel with non-stoichiometric composition  $\text{CuZr}_{1.86(1)}\text{S}_4$ , has been synthesized by the reaction of the constituent elements in an alkali metal halide flux and structurally characterized by single crystal X-ray diffraction techniques [28]. The title compound crystallizes in the rhombohedral space group  $R\bar{3}m$  [28]. This compound is isostructural with the rhombohedral modification of  $\text{CuTi}_2\text{S}_4$  (only the Zr(2) site has partial occupancy [28]). By using the concept of the critical irreducible representation (irrep), we establish the structure mechanism of a rhombohedral phase formation from the high symmetry cubic phase (parent phase). The first Brillouin zone of a face-centred cubic lattice contains four points of high symmetry, namely:  $\mathbf{k}_{11}(\Gamma)$ ,  $\mathbf{k}_{10}(X)$ ,  $\mathbf{k}_9(L)$  and  $\mathbf{k}_8(W)$  [29]. For these points there are stars of the following wavevectors:

$$\mathbf{k}_{11} = 0; \quad \mathbf{k}_{10} = \frac{1}{2}(b_1 + b_2); \quad \mathbf{k}_9 = \frac{1}{2}(b_1 + b_2 + b_3); \quad \mathbf{k}_8 = \frac{b_1}{4} - \frac{b_2}{4} + \frac{b_3}{2}.$$

Using the results of a group-theoretical analysis, we find that the phases with a space group  $R\bar{3}m$  can be generated by three-dimensional irrep  $\mathbf{k}_{11}(\tau_7) (\Gamma_5^+)^1 (1)$ , as well as six-dimensional irreps  $\mathbf{k}_{10}(\tau_1)(X_3) (4)$  and  $\mathbf{k}_{10}(\tau_3) (X_1) (4)$ , four-dimensional irreps  $\mathbf{k}_9(\tau_1) (L_1^+) (8, 2)$  and  $\mathbf{k}_9(\tau_4) (L_2^-) (8, 2)$ . The expression  $\mathbf{k}_j(\tau_i)$  means the star of wave vectors  $\mathbf{k}_j$ ,  $i$  – number corresponding irrep  $\tau$  for given star  $\mathbf{j}$  (according to [29]). The multiplication in the primitive cell volumes as a result of the  $Fd\bar{3}m \rightarrow R\bar{3}m$  phase transitions is shown in parentheses.

The results of the group-theoretical analysis show that the calculated distribution of the atoms on Wyckoff positions of the  $R\bar{3}m$ -phase is consistent with the experimental data [28] only in the case of phase generated by irrep  $\mathbf{k}_9(\tau_4) (L_2^-)$ . In Table 1 space groups of all possible low-symmetry phases, induced by irrep  $\mathbf{k}_9(\tau_4) (L_2^-)$ , and corresponding components of four-dimensional order parameter are given. A similar table was given earlier in the [25], but in this paper we supplemented it with secondary order parameters, which allow us to discuss the concept of multi-order on the rhombohedrally distorted spinel structure. Besides the change of primitive cell volumes as a result of the structural phase transitions ( $V/V_0$ ), vectors of the primitive cell translations ( $\mathbf{a1}$ ,  $\mathbf{a2}$ ,  $\mathbf{a3}$ ), structure formulas of low-symmetry phases are presented. The superscript index in the structural formula means the type of Wyckoff position according to International Tables for Crystallography [30]. Superscript on the brackets means the number of repetition of Wyckoff position in the structural formula.

<sup>1</sup>In parentheses, the notations are given for irreducible representations in accordance with Miller–Love.

Table 1: Low-symmetry crystal phases induced by irrep  $\mathbf{k}_9(\tau_4)$  ( $L_2^-$ ) of space group  $Fd\bar{3}m$

No	Critical OP	Noncritical OPs	Space group	$\frac{V}{V_0}$	Translations of primitive cell of spinel structure	Structural formula
1	(00 $\eta\eta$ )	$\Gamma_3^+(a, \sqrt{3}a)$ , $\Gamma_5^+(0, a, 0)$ , $L_3^-(0, 0; 0, 0; a, \frac{\sqrt{3}}{3}a; a, \frac{\sqrt{3}}{3}a)$ , $X_1(0, 0; a, 0; 0, 0)$	$Cmcm$ (No 63)	4	$2a_2 + 2a_3 - 2a_1$ , $2a_3 + 2a_1 - 2a_2$ , $2a_1 + 2a_2 - 2a_3$	$(A^c)^2 A_2^g$ $(B_2^g)^2 B_2^f B_2^c$ $(X_2^g)^4 (X_2^f)^2 X^h$
2	( $\eta\eta\eta\eta$ )	$\Gamma_2^-(a)$ , $L_1^+(a; a; a; a)$ , $X_1(a, a; a, a; a, a)$	$F\bar{4}3m$ (No 216)	8	$2a_2 + 2a_3 - 2a_1$ , $2a_3 + 2a_1 - 2a_2$ , $2a_1 + 2a_2 - 2a_3$	$A^a (A_4^e)^2 A_6^g A^b$ $(B_4^e)^2 (B_{12}^h)^2$ $(X_4^e)^4 (X_{12}^h)^4$
3	(00 $\eta$ )	$\Gamma_5^+(a, a, a)$	$R\bar{3}m$ (No 166)	2	$a_2 - a_1$ , $a_1$ , $2a_1 + 2a_2 + 2a_3$	$(A_{1/2}^c)^2$ $B_{1/4}^a B_{1/4}^b B_{3/2}^h$ $(X_{1/2}^c)^2 (X_{3/2}^h)^2$
4	( $\eta\eta\eta$ )	$\Gamma_5^+(a, a, a)$ , $L_1^+(a; 0; 0; 0)$ , $L_3^-(0, 0; a, \frac{\sqrt{3}}{3}a; -a, \frac{\sqrt{3}}{3}a$ ; $0, -\frac{2\sqrt{3}}{3}a)$ , $X_1(a, 0; a, 0; a, 0)$ , $X_3(a, -a; a, -a; a, -a)$	$R\bar{3}m$ (No 166)	8	$2a_3$ , $-2a_2$ , $6a_2 - 2a_1 - 2a_3$	$(A_{1/8}^c)^2 (A_{3/8}^h)^2$ $(B_{3/8}^h)^3 B_{1/8}^c$ $B_{3/8}^g B_{3/8}^f$ $(X_{3/8}^h)^6 X_{1/8}^c$ $X_{3/8}^c (X_{6/8}^i)^2$
5	( $\eta_1\eta_1\eta_2$ )	$\Gamma_3^+(a, 0)$ , $\Gamma_4^+(a, -a, 0)$ , $\Gamma_5^+(a, b, b)$ , $L_1^+(a; 0; 0; 0)$ , $L_3^+(a, 0; 0, 0; 0, 0; 0, 0)$ , $L_1^-(0; a; -a; 0)$ , $L_3^-(0, 0; a, b; -a, b; 0, c)$ , $X_1(a, 0; a, 0; b, 0)$ , $X_2(a, 0; -a, 0; 0, 0)$ , $X_3(a, -a; a, -a; b, -b)$ , $X_4(a, -a; -a, a; 0, 0)$	$C2/m$ (No 12)	8	$4a_2 - 2a_3$ , $2a_3$ , $2a_1 - 2a_2$	$(A_{1/8}^i)^4 (A_{2/8}^j)^2$ $(B_{2/8}^j)^4 (B_{1/8}^i)^4$ $B_{1/8}^h B_{1/8}^g$ $(X_{2/8}^j)^{12} (X_{1/8}^i)^8$
6	( $\eta_1\eta_2\eta_2\eta_2$ )	$\Gamma_5^+(a, a, a)$ , $\Gamma_2^-(a)$ , $\Gamma_4^-(a, a, a)$ , $L_1^+(a; b; b; b)$ , $L_3^+(0, 0; a, -\sqrt{3}a; a, \sqrt{3}a; -2a, 0)$ , $L_3^-(0, 0; a, \frac{\sqrt{3}}{3}a; -a, \frac{\sqrt{3}}{3}a; 0$ ; $-\frac{2\sqrt{3}}{3}a)$ , $X_1(a, b; a, b; a, b)$ , $X_4(a, a; a, a; a, a)$ , $X_3(a, -a; a, -a; a, -a)$	$R\bar{3}m$ (No 160)	8	$2a_1$ , $2a_1 - 2a_3$ , $6a_2 - 2a_1 - 2a_3$	$(A_{1/16}^a)^4 (A_{3/16}^b)^4$ $(B_{3/16}^b)^6 (B_{1/16}^a)^2$ $(B_{6/16}^c)^2$ $(X_{3/16}^b)^{12} (X_{1/16}^a)^4$ $(X_{6/16}^c)^4$

7	$(\eta_1\eta_1\eta_2\eta_2)$	$\Gamma_3^+(a, \sqrt{3}a),$ $\Gamma_5^+(0, a, 0),$ $\Gamma_2^-(a),$ $\Gamma_3^-(a, \sqrt{3}a),$ $\Gamma_4^-(a, 0, 0),$ $L_1^+(a; a; b; b),$ $L_3^+(a, -\sqrt{3}a; a, -\sqrt{3}a; b, -\sqrt{3}b;$ $b, -\sqrt{3}b),$ $L_3^-(a, \frac{\sqrt{3}}{3}a; a, \frac{\sqrt{3}}{3}a; b, \frac{\sqrt{3}}{3}b;$ $b, \frac{\sqrt{3}}{3}b),$ $X_1(a, a; b, c; a, a),$ $X_2(a, a; 0, 0; -a, -a),$ $X_3(a, 0; 0, 0; 0, -a),$ $X_4(0, a; 0, 0; a, 0)$	<i>Imm2</i> (No 44)	8	$2a_3,$ $2a_1 - 2a_2,$ $2a_1 + 2a_2 - 2a_3$	$(A_{1/16}^a)^2(A_{2/16}^c)^2A_{4/16}^e$ $(A_{2/16}^d)^2(A_{1/16}^b)^2$ $(B_{2/16}^c)^4(B_{2/16}^d)^4$ $(B_{4/16}^e)^4$ $(X_{2/16}^c)^8(X_{2/16}^d)^8$ $(X_{4/16}^e)^8$
8	$(0\eta_1\eta_2)$	$\Gamma_3^+(a, \sqrt{3}a),$ $\Gamma_4^+(0, a, a),$ $\Gamma_5^+(a, b, -a),$ $L_3^-(0, 0; 0, 0; a, \frac{\sqrt{3}}{3}a; b, \frac{\sqrt{3}}{3}b),$ $X_1(0, 0; a, 0; 0, 0),$ $X_4(0, 0; a, -a; 0, 0)$	<i>C2<sub>1/m</sub></i> (No 11)	4	$a_1 + a_2,$ $a_2 - a_1,$ $2a_3 - a_1 - a_2$	$(A_{1/4}^e)^4(B_{1/4}^e)^4$ $(B_{2/4}^f)^2$ $(X_{1/4}^e)^8(X_{2/4}^f)^4$
9	$(\eta_1\eta_2\eta_2\eta_3)$	$\Gamma_3^+(a, 0),$ $\Gamma_4^+(a, -a, 0),$ $\Gamma_5^+(a, b, b),$ $\Gamma_2^-(a),$ $\Gamma_3^-(a, 0),$ $\Gamma_4^-(a, a, b),$ $\Gamma_5^-(0, a, -a),$ $L_1^+(a; b; b; c),$ $L_2^+(0; a; -a; 0),$ $L_3^+(a, 0; b, c; b, -c; d, 0),$ $L_1^-(0; a; -a; 0),$ $L_3^-(0, a; b, c; -b, c; 0, d),$ $X_1(a, b; a, b; c, d),$ $X_2(a, b; -a, -b; 0, 0),$ $X_3(a, b; -b, -a; c, -c),$ $X_4(a, b; b, a; c, c)$	<i>Cm</i> (No 8)	8	$4a_2 - 2a_3,$ $2a_3,$ $2a_1 - 2a_2$	$(A_{1/16}^a)^8(A_{2/16}^b)^4$ $(B_{2/16}^b)^{12}(B_{1/16}^a)^8$ $(X_{2/16}^b)^{24}(X_{1/16}^a)^{16}$
10	$(\eta_1\eta_2\eta_3)$	$\Gamma_2^+(a),$ $\Gamma_3^+(a, b),$ $\Gamma_4^+(a, b, c),$ $\Gamma_5^+(a, b, c),$ $L_1^+(a; 0; 0; 0),$ $L_2^+(a; 0; 0; 0),$ $L_3^+(a, b; 0, 0; 0, 0; 0, 0),$ $L_1^-(0; a; b; c),$ $L_3^-(0, 0; a, b; c, d; e, f),$ $X_1(a, 0; b, 0; c, 0),$ $X_2(a, 0; b, 0; c, 0),$ $X_3(a, -a; b, -b; c, -c),$ $X_4(a, -a; b, -b; c, -c)$	<i>Pi</i> (No 2)	8	$2a_1,$ $2a_2,$ $2a_3$	$(A_{1/8}^i)^8$ $(B_{1/8}^i)^{16}$ $(X_{1/8}^i)^{32}$

11	$(\eta_1\eta_2\eta_3\eta_4)$	$\Gamma_2^+(a),$ $\Gamma_3^+(a, b),$ $\Gamma_4^+(a, b, c),$ $\Gamma_5^+(a, b, c),$ $\Gamma_1^-(a),$ $\Gamma_2^-(a),$ $\Gamma_3^-(a, b),$ $\Gamma_4^-(a, b, c),$ $\Gamma_5^-(a, b, c),$ $L_1^+(a; b; c; d),$ $L_2^+(a; b; c; d),$ $L_3^+(a, b; c, d; e, f; g, h),$ $L_1^-(a; b; c; d),$ $L_3^-(a, b; c, d; e, f; g, h),$ $X_1(a, b; c, d; e, f),$ $X_2(a, b; c, d; e, f),$ $X_3(a, b; c, d; e, f),$ $X_4(a, b; c, d; e, f)$	P1 (No 1)	8	$2a_1,$ $2a_2,$ $2a_3$	$(A_{1/16}^a)^{16}$ $(B_{1/16}^a)^{32}$ $(X_{1/16}^a)^{64}$
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Note.  $V/V_0$  is the change in the 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. The superscript on the brackets is the repetition number of the position.

### 3. Multi-order and structural mechanism formation of the rhombohedral modification

The structural mechanism for the formation of low-symmetry modifications of crystals is determined by interaction of all freedom degrees of a crystal, including lattice, charge, orbital and spin. The A-atoms occupy Wyckoff position  $8a$  (site symmetry  $\bar{3}m$ ), B-Wyckoff position  $16d$  (site symmetry  $\bar{4}3m$ ), X-Wyckoff position  $32e$  (site symmetry  $3m$ ) in the cubic  $Fd\bar{3}m$ -phase of normal spinel. Therefore structural formula of cubic spinel  $AB_2X_4$  is  $(A)^{8a}[B_2]^{16d}X_4^{32e}$  or applied to  $CuZr_{1.86(1)}S_4$  it is  $(Cu)^{8a}[Zr_{1.86(1)}]^{16d}S_4^{32e}$ . As a result of a hypothetical structural phase transition, the Wyckoff positions split. To find the splitting of the Wyckoff positions and calculate the structure of the rhombohedral phase, it is necessary to establish whether the critical irrep is included in the permutation, mechanical, magnetic and orbital representations of the spinel structure, as well as to elucidate the role of noncritical order parameters in the formation of a low-symmetry structure [24, 31–33].

The critical four dimensional irrep  $\mathbf{k}_9(\tau_4)$  ( $L_2^-$ ) enters into the mechanical representation and permutation representation of the spinel structure on Wyckoff positions  $8a$ ,  $16d$  and  $32e$  [24, 31–33], as well as in the  $e_g$ - and  $t_{2g}$ -orbital representations on Wyckoff position  $8a$  and  $16d$ . This means that the formation of a low-symmetry phase occurs according to a complex mechanism, including displacements of tetrahedral and octahedral cations, anions and as well as also ordering of all atom types. In addition, the formation of a rhombohedral phase can be accompanied by a charge and orbital ordering of tetrahedral and octahedral cations.

Group-theoretical analysis showed that the formation of the 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);
- quarternary anion ordering (order type 1:1:3:3).

As a result, the theoretical structural formula of a low-symmetry rhombohedral  $R\bar{3}m$ -spinel modification should be  $A_{1/2}^{2c}A_{1/2}^{2c}B_{1/4}^{1a}B_{1/4}^{1b}B_{3/2}^{6h}X_{1/2}^{2c}X_{1/2}^{2c}X_{3/2}^{6h}X_{3/2}^{6h}$  (the rhombohedral presentation) or  $A_{1/2}^{6c}A_{1/2}^{6c}B_{1/4}^{3a}B_{1/4}^{3b}B_{3/2}^{18h}X_{1/2}^{6c}X_{1/2}^{6c}X_{3/2}^{18h}X_{3/2}^{18h}$  (the hexahedral presentation). Attached to  $CuZr_{1.86(1)}S_4$  the latest structural formula is  $Cu(1)_{1/2}^{6c}Cu(2)_{1/2}^{6c}Zr(1)_{1/4}^{3a}Zr(2)_{1/4}^{3b}Zr(3)_{3/2}^{18h}S(1)_{1/2}^{6c}S(2)_{1/2}^{6c}S(3)_{3/2}^{18h}S(4)_{3/2}^{18h}$ . The derived theoretical structural formula exactly agrees with the experimental data [28]. It follows from the structural formula that in the structure of  $CuZr_{1.86(1)}S_4$  there are two structurally different copper atoms, three zirconium atoms, and four sulfur atoms. The structural difference between atoms of the same element can be associated with differences in charges, orientation and filling of orbitals with electrons, as well as other electronic characteristics of atoms. In particular, in  $CuZr_{1.86(1)}S_4$ , ordering of charges is possible, because copper, zirconium, sulfur atoms occupy some different Wyckoff positions in the rhombohedral spinel modification.

This theoretical result in principle agrees with the calculations [28]. The oxidation state of Cu atoms in the title compound is assigned +1, consistent with the Cu–S bond distances and the density of states. The calculated Madelung potentials and sums of bond valences show some difference for the three Zr positions, but this difference is not large, as

might be expected for the oxidation states of zirconium atoms with formal charges of 4+ and 3+ [27]. Charge distribution should be  $(\text{Cu}^+)_4\text{Zr}(1)^{4+}\text{Zr}(2)^{3+}\text{Zr}(3)_6^{3.5+}(\text{S}^{2-})_{16}$  according to the crystal bond lengths analysis and electronic structure calculations [28]. Our calculation predicts that copper atoms should differ from each other in physical characteristics, and possibly also in charges. Since the exact charges of metallic atoms are not known, we note that our calculations point to the fundamental possibility of orbital ordering in the formation of Zr(3)–Zr(3) bonds. The group-theoretical analysis predicted that at the formation of low-symmetric ordered  $R\bar{3}m$ -phase does not involve the rotations and tilts of tetrahedra and octahedra [31]. An important result of theoretical calculations is the prediction of the improper ferroelasticity of the rhombohedral phase, since the components of the secondary order parameter  $(\xi, \xi, \xi)$  induced by  $\mathbf{k}_{11}(\tau_7)$  ( $\Gamma_5^+$ ) (Table 1) are proportional to the shear components  $u_{xy}, u_{xz}, u_{yz}$  of the strain tensor  $u_{ij}$  [34]. Thus, the multi-order in the rhombohedral phase of  $\text{CuZr}_{1.86(1)}\text{S}_4$  is related to the lattice, charge, and possibly orbital degrees of freedom of the crystal. This multi-order causes the possibility of an improper ferroelasticity in the title compound.

Group-theoretical methods allow us to make an approximate estimate of free atomic parameters and atomic coordinates in the rhombohedral spinel modification [35, 36]. We emphasize that it is impossible to find the exact values of free atom parameters (“gliding” parameters) within the framework of the group-theoretical methods. For  $\text{CuZr}_{1.86(1)}\text{S}_4$  using the ISOTROPY program we get the formula for approximate estimate of the coordinates of atoms:  $\text{Cu}(1)^{6c}$  ( $z' = 5/16$ ),  $\text{Cu}(2)^{6c}$  ( $z' = 3/16$ ),  $\text{Zr}(1)^{3a}$ ,  $\text{Zr}(2)^{3b}$ ,  $\text{Zr}(3)^{18h}$  ( $x' = 1/6, z' = 7/12$ ),  $\text{S}^{18h}$  ( $x' = -1/6 - 4/3x, z' = 1/6 - 1/6x$ ),  $\text{S}^{18h}$  ( $x' = 1/6 - 4/3x, z' = 1/3 - 1/6x$ ),  $\text{S}^{6c}$  ( $z' = 1/4 - 1/2x$ ),  $\text{S}^{6c}$  ( $z' = 1/4 + 1/2x$ ). The superscript index in this formula are the atom coordinates in agreement with International Tables for Crystallography; the values of  $x'$  and  $z'$  are the values of the adjusted parameters of the corresponding Wyckoff positions,  $x$  – theory parameter for the given Wyckoff position. Note that for some positions of atoms, good agreement is obtained between the theoretical and experimental coordinates of atoms (Cu(1), Cu(2), Zr(1), Zr(2)), and for some atoms (for example, Zr(3)) the resulted theoretical and experimental data do not agree. The quantitative discrepancy between the theoretical and experimental coordinates of some atoms can appear due to several reasons. We note only three of them related to the title compounds.

- (1) *Sample metastability.* In metastable structures, atoms (all atoms or only a part of them) have coordinates that differ from the coordinates of atoms in thermodynamically stable structures. The possible metastability of  $\text{CuZr}_{1.86(1)}\text{S}_4$  is indicated by the fact that the crystal structure of the title compound critically depends on the technology of its manufacturing.
- (2) *Partial atomic occupancy of Wyckoff positions.* The group-theoretical calculations do not take into account the partial occupation of the corresponding Wyckoff positions by some atoms (in the case of  $\text{CuZr}_{1.86(1)}\text{S}_4$ , Zr(2) atoms partially occupy the 3b Wyckoff position [28]).
- (3) *The role of noncritical representations in low-symmetry structure formation.* A critical irrep completely defines the symmetry of the low-symmetry phase in vicinity transition point  $T_c$ . The role of noncritical degrees of freedom near the phase transition temperature is insignificant. Far from the  $T_c$ , the contribution of noncritical degrees of freedom to the formation of a low-symmetry structure can become significant [35]. And therefore, taking into account these degrees of freedom is necessary for an adequate representation of the calculated structure. A method for finding noncritical atomic displacements and noncritical orderings was proposed in [33]. According to Landau theory of phase transition the components of the critical and noncritical (secondary) order parameters are proportional to  $|T - T_c|^{1/2}$  and  $|T - T_c|^{n/2}$  respectively. Here  $n$  is the least direct symmetrized power of the critical irrep, which contains the noncritical irrep. The second direct symmetrized power of the critical irrep  $\mathbf{k}_9(\tau_4)$  ( $L_2^-$ ) ( $n = 2$ ) contains the noncritical irrep  $\mathbf{k}_{11}(\tau_7)$  ( $\Gamma_5^+$ ). Our group-theoretical calculation shows that in case of the  $\text{CuZr}_{1.86(1)}\text{S}_4$ , noncritical (secondary) order parameter  $(\xi, \xi, \xi)$  generated by  $\mathbf{k}_{11}(\tau_7)$  ( $\Gamma_5^+$ ) must play an important role in the structure formation. The critical irrep  $\mathbf{k}_{11}(\tau_7)$  ( $\Gamma_5^+$ ) is included in the mechanical representation constructed for the 8a and 32e sites of the parent spinel structure and the permutation representation constructed for the 16d and 32e sites. This means that the structure of the low-symmetry ordered  $R\bar{3}m$ -phase is formed as a result of the additional displacements of Cu and S atoms and additional ordering of Zr cations and S anions (in both cases the type of order is 1:3). Our theory predicts a linear dependence of  $|T - T_c|$  on the Cu and S atoms displacements and weak superstructure reflexes, corresponding to 1:3 ordering of the Zr cations and 1:3 ordering of the S anions. All three of the above factors have a significant impact on the formation of the  $\text{CuZr}_{1.86(1)}\text{S}_4$  rhombohedral structure.

#### 4. Results of crystal-chemical design and general discussion

One peculiar feature of the  $\text{CuZr}_{1.86(1)}\text{S}_4$  rhombohedral structure is metal clustering. In contrast to the  $\text{AlV}_2\text{O}_4$  rhombohedral structure, in which the formation of heptamers [20] (or trimers [21]) occurs by vanadium atoms ordering, located in octahedral sites of the initial cubic spinel, in the formation of metal clusters in  $\text{CuZr}_{1.86(1)}\text{S}_4$  rhombohedral structure not only the octahedral zirconium atoms but also tetrahedral atoms of copper takes part (Figs. 2, 3).

Atoms of Cu(2) and Zr(3) form “bunch” of dimers (Fig. 3). Each “bunch” consists of three [Cu(2)–Zr(3)]-dimers which are joined by common Cu(2)-atom. Each Cu(2) atom is surrounded by three Zr(3) atoms, resulting in three Cu(2)–Zr(3) interatomic distances of 2.937 Å. The shortest Cu–Zr distance in cubic spinel is much longer and equals 4.304 Å.

This distance is too large for a significant interaction, while Cu(2)–Zr(3) interatomic distance in the rhombohedral form of  $\text{CuZr}_{1.86(1)}\text{S}_4$  is the shortest among all the bond lengths of the metal-metal. Note that Zr(1)- and Zr(3)-atoms also form [Zr(1)–Zr(3)]-dimers, but with a much larger interatomic distance 3.787 Å (on Fig. 4 they are shown blue). Thus, the “bunches” of [Cu(2)–Zr(3)]-dimers are the smallest size metal clusters.

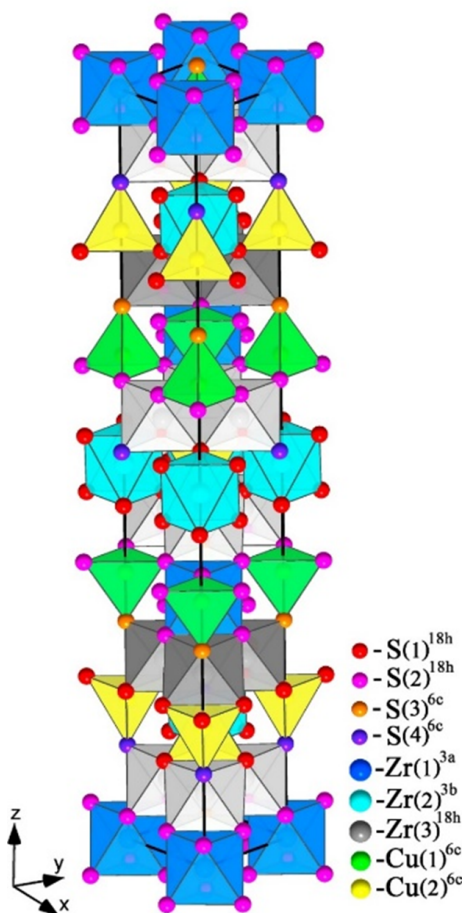


FIG. 2. Low-symmetry ordered  $R\bar{3}m$ -structure of  $\text{CuZr}_{1.86(1)}\text{S}_4$ . Polyhedral presentation in the form of  $\text{Cu}(2)[\text{S}(3)_3\text{S}(2)]$  (yellow) and  $\text{Cu}(1)[\text{S}(4)_3\text{S}(1)]$  (green) tetrahedra and  $\text{Zr}(1)[\text{S}(3)_6]$  (dark blue),  $\text{Zr}(2)[\text{S}(4)_6]$  (blue),  $\text{Zr}(3)[\text{S}(1)\text{S}(2)\text{S}(3)_2\text{S}(4)_2]$  (gray) octahedral is presented.

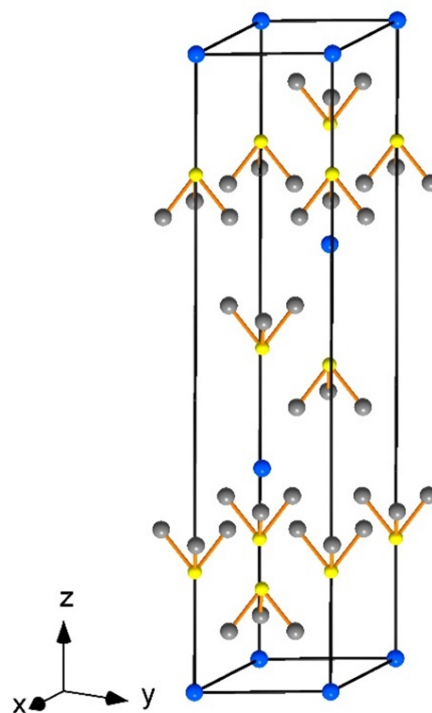


FIG. 3. “Bunch” of [Cu(2)–Zr(3)]-dimers

On the kagome lattice, there are two kinds of Zr(3)–Zr(3) bonds (zirconium dimers  $[\text{Zr}(3)_2]$ ) with different bond lengths: the shorter (black) is 3.579 Å and the longer (dark blue) is 3.773 Å (Fig. 4). These dimers alternate in the kagome lattice (Fig. 4). It is interesting to note, that distance Zr–Zr in the cubic form of  $\text{CuZr}_{1.86(1)}\text{S}_4$  is equal to 3.670 Å. Zr(3)-atoms, belonging to the “bunch”, form two types of  $[\text{Zr}(3)_3]$ -trimers with interatomic distances  $\text{Zr}(3)\text{–Zr}(3) = 3.579$  Å and  $\text{Zr}(3)\text{–Zr}(3) = 3.773$  Å (Fig. 4). Alternating  $[\text{Zr}(3)_3]$ -trimers, having short and long interatomic distances  $\text{Zr}(3)\text{–Zr}(3)$ , form a kagome layer (Fig. 4). These trimers are at the basis of four types of tetrahedra. Each trimer, formed by bonds  $\text{Zr}(3)\text{–Zr}(3)$ , is the basis for the metal  $[\text{Cu}(2)\text{Zr}(3)_3]$ -tetrahedra and  $[\text{Cu}(1)\text{Zr}(3)_3]$ -tetrahedra with S(3)-atoms in the centre (Fig. 4). Each trimer, formed by more longer bonds  $\text{Zr}(3)\text{–Zr}(3)$ , is the basis for the metal  $[\text{Zr}(1)\text{Zr}(3)_3]$ -tetrahedra and  $[\text{Cu}(2)\text{Zr}(3)_3]$ -tetrahedra with S(4)-atoms in the centre (Fig. 4).

There are two different types of kagome-layers binding in the structure of title compound  $\text{CuZr}_{1.86(1)}\text{S}_4$ . The first type of binding between the displaced kagome-layers relative to each other is realized by means of metal clusters – heptamers  $[\text{Zr}(1)\text{Zr}(3)_6]$  (Fig. 4). The second type of binding kagome-layers is realized between the undisplaced kagome-layers relative to each other by means of  $[\text{Cu}(2)\text{Zr}(3)_3]$ -tetrahedra and S(4) $[\text{Cu}(2)\text{Zr}(3)_3]$ -tetrahedra with S(4)-atoms in the centre (Fig. 5).

Displaced and undisplaced kagome layers alternate with each other in the structure of  $\text{CuZr}_{1.86(1)}\text{S}_4$  rhombohedral spinel modification. Note that there is only one type of kagome-layers binding in the structure of the parent (cubic spinel) phase (Fig. 1). In the rhombohedral structure of  $\text{CuZr}_{1.86(1)}\text{S}_4$ , it is possible to distinguish Zr(1)-heptamers, which are

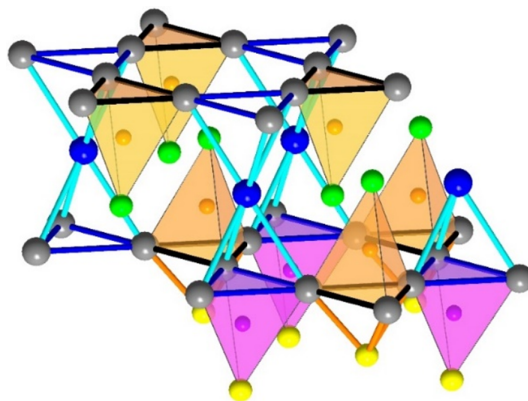


FIG. 4. Two types of  $[\text{Zr}(3)_2]$ -dimers (dark blue and black) and  $[\text{Zr}(3)_3]$ -trimers,  $[\text{Cu}(2)\text{Zr}(3)_3]$ - and  $[\text{Zr}(1)\text{Zr}(3)_3]$ -tetrahedral metal clusters,  $\text{S}(3)[\text{Cu}(1)\text{Zr}(3)_3]$ - (light brown) and  $\text{S}(4)[\text{Cu}(2)\text{Zr}(3)_3]$ - (pink) tetrahedral clusters are shown

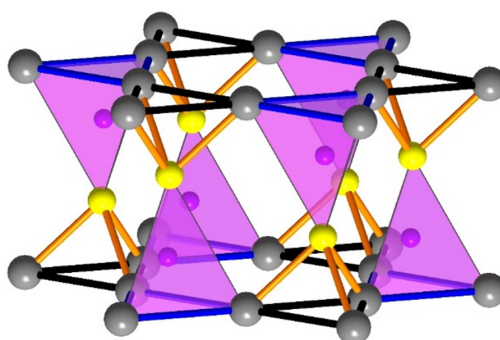


FIG. 5. Binding between kagome-layers with the help  $\text{S}(4)[\text{Cu}(2)\text{Zr}(3)_3]$ -tetrahedra

analogs of V-heptamers in the structure of  $\text{AlV}_2\text{O}_4$  [20]. Here, all the  $\text{Zr}(1)$  atoms are sandwiched by two  $[\text{Zr}(3)_3]$ -trimers (Fig. 4), but none of the  $\text{Zr}(2)$  atoms are sandwiched by two  $[\text{Zr}(1)_3]$ -trimers.  $\text{Zr}(2)$  atoms are sandwiched by two  $[\text{S}(1)_3]$ -trimers, forming heptamer  $[\text{Zr}(2)\text{S}(1)_6]$  (Fig. 6).

In this heptamer, the interatomic distances  $\text{S}(1)\text{--}\text{S}(1)$  and  $\text{Zr}(2)\text{--}\text{S}(1)$  are 3.570 and 2.583 Å, respectively. This formula means that the  $\text{Zr}(1)^{4+}$  ion has no  $t_{2g}$  orbitals, i.e. there are no chemical bonding between  $\text{Zr}(1)$ - and  $\text{Zr}(3)$ -atoms. Therefore, the formation of Zr-heptamers is improbable. Besides the calculated densities of states of rhombohedral modification show that  $\text{Cu}(1)\text{--}\text{Zr}(3)$  and  $\text{Zr}(3)\text{--}\text{Zr}(3)$  interactions in “bunch” of dimers and  $[\text{Zr}(3)_3]$ -trimers (with interatomic distances  $\text{Zr}(3)\text{--}\text{Zr}(3)$  3.579 Å) have bonding character [28].

The nonstoichiometry of Zr deficient rhombohedrally distorted spinel related compound,  $\text{CuZr}_{1.86(1)}\text{S}_4$ , has no effect on the calculated structural formula and, consequently, on the structural motif of the rhombohedral phase (Figs. 2, 3). Nonstoichiometry leads to the fact that a part of the Wyckoff positions occupied by zirconium atoms in the rhombohedral

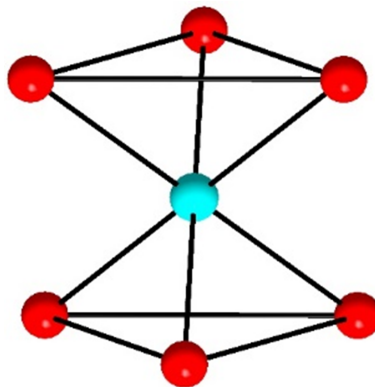


FIG. 6. The  $[\text{Zr}(2)\text{S}(1)_6]$ -heptamer



phase are vacant. This means that in a nonstoichiometric compound, the number of Zr-containing nanoclusters will decrease compared to the idealized stoichiometric structure, but their types will remain unchanged.

## 5. Conclusions

The main result of the study is the establishing of multi-order in the  $\text{CuZr}_{1.86(1)}\text{S}_4$  rhombohedral structure which associate with the nanocluster formation (dimers, trimers, and a unique type of clusters – “bunch” of dimers) according to a complex mechanism, including ordering and displacement of all atoms, charge ordering, and, possibly, orbital ordering in the  $[\text{Zr}(3)]_3$ -trimers. The group-theoretical analysis made it possible to predict the possible improper ferroelasticity of  $\text{CuZr}_{1.86(1)}\text{S}_4$  rhombohedral phase. It is also important to note that only two substances are known among all spinels, namely,  $\text{CuTi}_2\text{S}_4$  [25] and  $\text{CuZr}_{1.86(1)}\text{S}_4$ , which form metal cluster “bunch” of dimers whose atoms are simultaneously part of two frustrating sublattices<sup>2</sup> of the crystal structure (metal clusters in all known materials with a pyrochlore sublattice formed by atoms of only one geometrically frustrating sublattice). Therefore, “bunch” of  $[\text{Cu}(1)\text{--Zr}(3)]$ -dimers, which are metallic “molecules”, represent a new type of self-organization of atoms in crystals. This means that it is possible to rationally design new materials with unusual physical properties based on  $R\bar{3}m$  ordered spinels. Further studies of the physical properties of solid solutions based on  $R\bar{3}m$  ordered spinels, as well as their study under pressure, may lead to the discovery of their unusual physical properties.

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<sup>2</sup>The A-site ions ( $\text{Cu}^+$ ) are arranged in a diamond lattice. The A-site as well as the B-site cations in the spinel structure form lattices prone to strong frustration effects. The spinel structure exhibits very unusual ground states due to geometric frustration, the strength of which depends on the ratio of exchange interactions between and within the sublattices of two interpenetrating face-centered cubic lattices.

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