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## Phenomenological Thermodynamics and Structure Formation Mechanism of $\text{CuTi}_2\text{S}_4$ Rhombohedral Phase

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The theory of structural phase transition in  $\text{CuTi}_2\text{S}_4$  is proposed. The symmetry of order parameter, thermodynamics and mechanism of the atomic structure formation of 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 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 were named «bunch» of dimers. «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.

**Key words:** rhombohedral thiospinel, dimers, trimers, structural mechanism, phase diagram

**Synopsis.** The theory of the structural phase transition in  $\text{CuTi}_2\text{S}_4$  is proposed

## 1. Introduction

Copper-containing thiospinels exhibit a wide variety of physical properties that make them interesting from a scientific point of view [1-3]. For example, large negative magnetoresistance is observed in ferromagnetic thiospinel compound  $\text{CuCrZrS}_4$  [4]. The other spinels  $\text{CuRh}_2\text{S}_4$  and  $\text{CuRh}_2\text{Se}_4$  are superconductors [5-9]. 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 [10]. 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 [11-14].

Among copper-thiospinels  $\text{CuTi}_2\text{S}_4$  causes a great interest in 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 [15]. Below 5 K, the copper-thiospinel transforms into a spin singlet state [15]. The cubic thiospinel  $\text{CuTi}_2\text{S}_4$  can be formally described by 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  $\text{Ti}^{4+}$ ) [1]. The electronic, magnetic and structural properties of this compound are, however, not sufficiently understood at present.

There is another reason interest to  $\text{CuTi}_2\text{S}_4$ : three-dimensional geometrically frustrated magnets, which have two-dimensional kagome- and triangular-sublattices, is recently focused on a quantum spin liquid and/or heavy fermion-like states. It is assumed that such situation is realized in  $\text{CuTi}_2\text{S}_4$  [16].

The structure  $\text{CuTi}_2\text{S}_4$  depends on the method of synthesis. According to [17] the  $\text{CuTi}_2\text{S}_4$  compound has 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 8.3K [17]. Hence according to [18]  $\text{CuTi}_2\text{S}_4$  has the low-symmetry rhombohedral spinel modification with centrosymmetric space group  $R\bar{3}m$  which is irreversibly transformed into the cubic spinel at temperatures above 450°C [18]. Kinetically stabilized rhombohedral modification of  $\text{CuTi}_2\text{S}_4$  has been synthesized by the reaction of the constituent elements using eutectic alkali metal halide fluxes [18]. 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/formula unit [18].

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. Explain this thesis. The structure of  $R\bar{3}m$ -modification of  $\text{CuTi}_2\text{S}_4$  has atom distributions on Wyckoff positions such as atom distributions in the structure of high-order structure of  $\text{AlV}_2\text{O}_4$ . This high-order structure comprises a complex «molecular» clusters – V-heptamers [19]. Such large building blocks as V-heptamers are a consequence of cooperation between charge, spin and orbital degrees of freedom of the V ions [19, 20]. 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 spinel structure. In this paper, we mainly focus on the self-organization of atoms. We are first studying this question with the help of group-theoretical, thermodynamical and structural methods of the modern theory of phase transitions. These methods were described earlier in detail [21-29]. We have also checked the separate results obtained by our methods by means of the ISOTROPY program [30, 31]. The problem of self-organization of charges, spins and orbitals in  $R\bar{3}m$ -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 a group-theoretical analysis of the phase transitions occurring according to one critical irreducible representation (irrep) in the group  $\text{Fd}\bar{3}\text{m}$ , which satisfy the Lifshitz criterion [32], we find that the space group  $\text{R}\bar{3}\text{m}$  may be generated 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), 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 [33]:  $\mathbf{k}_j(\tau_i)$  – star of wave vectors  $\mathbf{k}_j$ ,  $i$  – number corresponding irrep  $\tau$  for given star  $\mathbf{j}$ . The multiplication in the primitive cell volumes as a result of phase transitions from high-symmetry  $\text{Fd}\bar{3}\text{m}$ -phase to low-symmetry  $\text{R}\bar{3}\text{m}$ -phase is shown in parentheses.

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

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 of 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
$\mathbf{k}_{10}(\tau_1)$	$\varphi \varphi \varphi \varphi \varphi$	4	1(4):3m + 1(12):m	1(2): m + 1(6):2/m +1(12):m + 1(12):2	1(4):3m + 3(12):m + 1(24):1
$\mathbf{k}_{10}(\tau_3)$	$\varphi \varphi \varphi \varphi \varphi$	4	1(4):3m + 1(12):m	1(2): m + 1(6):2/m +1(12):m + 1(12):2	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(1): m + 2(3):2/m +2(6):m + 1(12):1	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

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  $Z_B(\text{R}\bar{3}\text{m}) = 12$ , where  $Z_B$  is the number of formula units in the Bravais cell [18]. The basis vectors of the unit cell  $A_1, A_2, A_3$  of rhombohedral  $\text{R}\bar{3}\text{m}$ -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 spinel contains two formula units; therefore, the primitive cell volume for the rhombohedral phase is larger than the primitive-cell volume for cubic spinel by a factor of 2, i.e. it contains four formula units. The result: for space group  $\text{Fd}\bar{3}\text{m}$   $Z_P = 2$ ,  $Z_B = 8$ , for space group  $\text{R}\bar{3}\text{m}$   $Z_P = 4$ ,  $Z_B = 12$ . Hereafter  $Z_P$  is the number of formula units in the primitive cell. These theoretical results also are consistent with experimental data [18].

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 notation Stokes & 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  $\text{Fd}\bar{3}\text{m}$  group symmetry, forms a point group of order 384 in four-dimensional space. The OP transformation properties are given by the following generator matrices:

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

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  $\text{Fd}\bar{3}\text{m}$  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 equation (1) the generators of irrep  $\mathbf{k}_9(\tau_4)$  of  $\text{Fd}\bar{3}\text{m}$  group symmetry are given. The remaining irrep  $\mathbf{k}_9(\tau_4)$  matrices corresponding to other elements of  $\text{Fd}\bar{3}\text{m}$  group symmetry can be obtained as a result of multiplication of the above-mentioned matrices. Designations for symmetry elements of the  $\text{Fd}\bar{3}\text{m}$  space group are given according to Kovalev [33].

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. As well as 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 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  $\text{CuTi}_2\text{S}_4$  and structurally related materials. The list of low-symmetry phases (Table 2) is consistent with the results obtained in [34].

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

№	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	$2a_2+2a_3-2a_1,$ $2a_3+2a_1-2a_2,$	$(A^c)^2A_2^g(B_2^g)^2B_2^fB_2^c(X_2^g)^4(X_2^f)^2X^h$

				$2a_1+2a_2-2a_3$	
2	$(\eta \eta \eta \eta)$	$F\bar{4}3m$ (N216)	8	$2a_2+2a_3-2a_1,$ $2a_3+2a_1-2a_2,$ $2a_1+2a_2-2a_3$	$A^a(A^e_4)^2A^g_6A^b(B^e_4)^2(B^h_{12})^2(X^e_4)^4(X^h_{12})^4$
3	$(0 0 0 \eta)$	$R\bar{3}m$ (N166)	2	$a_2-a_1, a_1,$ $2a_1+2a_2+2a_3$	$(A^c_{1/2})^2B^a_{1/4}B^b_{1/4}B^h_{3/2}X^c_{1/2}(X^h_{3/2})^2$
4	$(0 \eta \eta \eta)$	$R\bar{3}m$ (N166)	8	$2a_3,-2a_2,$ $6a_2-2a_1-2a_3$	$(A^c_{1/8})^2(A^h_{3/8})^2(B^h_{3/8})^3B^c_{1/8}B^g_{3/8}B^f_{3/8}(X^h_{3/8})^6X^c_{1/8}X^c_{3/8}(X^i_{6/8})^2$
5	$(0 \eta_1 \eta_1 \eta_2)$	$C2/m$ (N12)	8	$4a_2-2a_3, 2a_3,$ $2a_1-2a_2$	$(A^i_{1/8})^4(A^l_{2/8})^2(B^j_{2/8})^4(B^i_{1/8})^4B^h_{1/8}B^g_{1/8}(X^j_{2/8})^{12}(X^i_{1/8})^8$
6	$(\eta_1 \eta_2 \eta_2 \eta_2)$	$R3m$ (N160)	8	$2a_1, 2a_1-2a_3,$ $6a_2-2a_1-2a_3$	$(A^a_{1/16})^4(A^b_{3/16})^4(B^b_{3/16})^6(B^a_{1/16})^2(B^c_{6/16})^2$ $(X^b_{3/16})^{12}(X^a_{1/16})^4(X^c_{6/16})^4$
7	$(\eta_1 \eta_1 \eta_2 \eta_2)$	$Imm2$ (N44)	8	$2a_3, 2a_1-2a_2,$ $2a_1+2a_2-2a_3$	$(A^a_{1/16})^2(A^c_{2/16})^2A^e_{4/16}(A^d_{2/16})^2(A^b_{1/16})^2$ $(B^c_{2/16})^4(B^d_{2/16})^4(B^e_{4/16})^4(X^c_{2/16})^8(X^d_{2/16})^8$ $(X^e_{4/16})^8$
8	$(0 0 \eta_1 \eta_2)$	$C2_1/m$ (N11)	4	$a_1+a_2, a_2-a_1,$ $2a_3-a_1-a_2$	$(A^e_{1/4})^4(B^c_{1/4})^4(B^f_{2/4})^2(X^e_{1/4})^8(X^f_{2/4})^4$
9	$(\eta_1 \eta_2 \eta_2 \eta_3)$	$Cm$ (N8)	8	$4a_2-2a_3, 2a_3,$ $2a_1-2a_2$	$(A^a_{1/16})^8(A^b_{2/16})^4(B^b_{2/16})^{12}(B^a_{1/16})^8(X^b_{2/16})^{24}(X^a_{1/16})^{16}$
10	$(0 \eta_1 \eta_2 \eta_3)$	$Pi$ (N2)	8	$2a_1, 2a_2, 2a_3$	$(A^i_{1/8})^8(B^i_{1/8})^{16}(X^i_{1/8})^{32}$
11	$(\eta_1 \eta_2 \eta_3 \eta_4)$	$P1$ (N1)	8	$2a_1, 2a_2, 2a_3$	$(A^a_{1/16})^{16}(B^a_{1/16})^{32}(X^a_{1/16})^{64}$

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:

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

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

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

$$J_4 = \eta_1^2\eta_2^2\eta_3^2\eta_4^2$$

The invariants basis (2) was constructed using the algorithm described in [35]. A phenomenological thermodynamic model of phase transitions will be built taking into account thermodynamic potential stability [36-39]. The term «stable» refers to the potential that allows us to construct a phase diagram that does not change at appearing of 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 «stable» thermodynamic potential it should be specified the type of multi-critical point [37]. 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:

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

The potential (3) at  $b_2 > 0$  and  $b_{12} > 0$  on plane  $(a_1, a_2)$  describes a phase transition into  $R\bar{3}m$ -phase. As in the thermodynamic potential (3) there is no an 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 to the line of phase transitions of the first order. It is important to emphasize that the first order of the phase transition from  $Fd\bar{3}m$ -phase to  $R\bar{3}m$ -phase at  $a_2 < 0$  caused by sixth degree of order parameters components but not by the symmetry of the system. The irreversibility of the phase transition in  $CuTi_2S_4$  established experimentally [18] 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 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 normal spinel. The structural formula of cubic  $Fd\bar{3}m$ -spinel is  $(Cu)^{8a}[Ti_2]^{16d}S_4^{32e}$ .

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  $32e$  [21-24, 27]. This means that the low-symmetry phase formation is connected with displacements of tetrahedral and octahedral cations and anions and also with ordering of all atom types. Group-theoretic analysis showed that the formation of the  $CuTi_2S_4$  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);
- quarternary 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  $A^{2c}_{1/2}A^{2c}_{1/2}B^{1a}_{1/4}B^{1b}_{1/4}B^{6h}_{3/2}X^{2c}_{1/2}X^{2c}_{1/2}X^{6h}_{3/2}X^{6h}_{3/2}$ . (the rhombohedral presentation) or  $A^{6c}_{1/2}A^{6c}_{1/2}B^{3a}_{1/4}B^{3b}_{1/4}B^{18h}_{3/2}X^{6c}_{1/2}X^{6c}_{1/2}X^{18h}_{3/2}X^{18h}_{3/2}$  (the hexahedral presentation). Attached to  $CuTi_2S_4$  latest structural formula is  $Cu(1)^{6c}_{1/2}Cu(2)^{6c}_{1/2}Ti(1)^{3a}_{1/4}Ti(2)^{3b}_{1/4}Ti(3)^{18h}_{3/2}S(1)^{6c}_{1/2}S(2)^{6c}_{1/2}S(3)^{18h}_{3/2}S(4)^{18h}_{3/2}$ . Our theoretical structural formula agrees with experimental data [18].

Note that the  $CuTi_2S_4$  compound under consideration can have charge ordering in principle, because copper and titanium atoms, being in the Wyckoff positions  $8a$  and  $16d$  of 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 spinel structure. We used the value of the free parameters for Wyckoff positions atoms in rhombohedral spinel modification (which were taken from [18]) in order to build the  $R\bar{3}m$ -spinel structure. The results of theoretical calculations of the  $CuTi_2S_4$  atom structure are given below (Fig. 2).

### 2.4. Metal clusters in the structure of the $CuTi_2S_4$

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 compound (Fig. 2). This com-



pound is isostructural with the  $\text{CuZr}_{1.86(1)}\text{S}_4$  [40], with rhombohedral modification of  $\text{AlV}_2\text{O}_4$  [20] and with phase of high pressure of  $\text{LiV}_2\text{O}_4$  [41].

One 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 vanadium atoms ordering, located in octahedral sites of the initial cubic spinel, in the formation of metal clusters in  $\text{CuTi}_2\text{S}_4$  rhombohedral structure takes part not only the octahedral titanium atoms but also tetrahedral atoms of copper (Fig. 3).

Atoms of Cu(1) and Ti(3) form «bunch» of dimers (Fig. 3, 4). Each «bunch» consists of three [Cu(1)–Ti(3)]-dimers which are joined by 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 cubic spinel is much longer and equals 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 in the rhombohedral form.

On the kagome lattice, there are two kinds of Ti(3) - Ti(3) bonds (titanium dimers  $[\text{Ti}(3)_2]$ ) with different bond lengths: the shorter (dark blue) is 3.419 Å and the longer (red) is 3.606 Å (Fig. 5a, b). These dimers alternate in the kagome lattice (Fig. 5a). 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 trimers  $[\text{Ti}(3)_3]$  with interatomic distances Ti(3) - Ti(3) = 3.419 Å (Fig. 5a) and Ti(3) - Ti(3) = 3.606 Å (Fig. 3, 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:  $[\text{Cu}(1)\text{Ti}(3)_3]$  and  $[\text{Ti}(1)\text{Ti}(3)_3]$ . They have the opposite orientation (antiparallel) relative to the kagome-plane (Fig. 5b).

Each trimmer, formed by bonds Ti(3) - Ti(3), is the basis for the metal tetrahedron with the shortest bonds:  $[\text{Cu}(1)\text{Ti}(3)_3]$  and  $[\text{S}(2)\text{Cu}(2)\text{Ti}(3)_3]$  (Fig. 5c). Each trimer, formed by more longer 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 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 is an analog of V- heptamers in the structure of  $\text{AlV}_2\text{O}_4$  [19] (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)-atom are sandwiched by two  $[\text{S}(4)_3]$ -trimers and S(4) atoms constitute also one heptamer  $[\text{Ti}(2)\text{S}(4)_6]$  (Fig. 6b). But this S(4)-heptamer is not an analog 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, d) and sulfur atoms (Fig. 6c, d).

Previously, authors [18] suggested that the valence states of atoms in the  $\text{CuTi}_2\text{S}_4$  rhombohedral form should be  $(\text{Cu}^+)_4\text{Ti}(1)^{4+}\text{Ti}(2)^{3+}\text{Ti}(3)^{3.5+}_6(\text{S}^{2-})_{16}$  according to on 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 «bunch» of dimers and trimers  $[\text{Ti}(3)_3]$  (with interatomic distances Ti(3) - Ti(3) = 3.419 Å) have bonding character [18].

### 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 at the 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 [18]. We found that in  $\text{CuTi}_2\text{S}_4$  rhombohedral structure there are only one type of Ti-heptamers such as V-heptamers in  $\text{AlV}_2\text{O}_4$  [20]. But these heptamers have very large bond lengths and therefore cannot be considered as metal «molecules» in  $\text{CuTi}_2\text{S}_4$  rhombohedral structure.

We first established the existence of «bunch» of [Cu(1)-Ti(3)]-dimers, two types of Ti(3)-trimers [Ti(3)<sub>3</sub>] and two types tetrahedral clusters ([Cu(1)Ti(3)<sub>3</sub>] and [Ti(1)Ti(3)<sub>3</sub>]). Of particular interest are metal nanostructures: [Cu(1)-Ti(3)]-dimers, trimers [Ti(3)<sub>3</sub>] with the shorter bond lengths and «bunch» of [Cu(1)-Ti(3)]-dimers. The metallic dimers and trimers in geometrically frustrated structures (for examples dimmers:  $\text{MgTi}_2\text{O}_4$  [43-45],  $\text{CuTe}_2\text{O}_5$  [46, 47],  $\text{VO}_2$  [48],  $\text{CuGeO}_3$  [49]; trimers:  $\text{LiVO}_2$  [50],  $\text{LiVS}_2$  [51],  $\text{NaV}_6\text{O}_{10}$  [52],  $\text{BaV}_{10}\text{O}_{15}$  [53-56],  $\text{SrV}_8\text{Ga}_4\text{O}_{19}$  [57],  $\text{AV}_{13}\text{O}_{18}$  (A = Ba, Sr) [58],  $\text{A}_2\text{V}_{13}\text{O}_{22}$  (A = Ba, Sr) [59],  $\text{Ba}_4\text{Ru}_3\text{O}_{10}$  [60]) has long been known. The formation of «bunch» of [Cu(1)-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 ( $\text{Fd}\bar{3}m$  and  $\text{R}\bar{3}m$ ) may occur as a result of both second and first-order phase transitions in the vicinity of the tricritical point. In case of  $\text{CuTi}_2\text{S}_4$  we propose that phase transition of the first order close to the second order in the vicinity of 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 [42]. This result is based on our calculations of the phase diagram and an experimental fact of the irreversibility of the phase transition [18].

It is interesting to note that the magnetization of some spinels normally takes place along [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 a Pauli paramagnets [18]. The Pauli susceptibility of the  $\text{R}\bar{3}m$  form is larger than that of the thiospinel in quantitative agreement with the LMTO-ASA band structure calculations [18]. The authors [18] point out that a transition to the ferromagnetic state might occur below the temperature range investigated (2-300 K). The magnetic structure of the  $\text{CuTi}_2\text{S}_4$  near 2K remains unknown.

#### 4. Conclusions

We first proposed a theory of the structural phase transition in  $\text{CuTi}_2\text{S}_4$ , built possible phase diagram and established a structural mechanism of the low-symmetry rhombohedral modification formation from 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 conditions of metallic nanoclusters stability. For this it is necessary to make the 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  $\text{CuTi}_2\text{S}_4$ .

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## Captions to figures

Michail V. Talanov, Vladimir. B. Shirokov, Valery M. Talanov  
 Phenomenological Thermodynamics and Structure Formation Mechanism of  $\text{CuTi}_2\text{S}_4$   
 Rhombohedral Phase

Figure 1. Phase diagram described by the thermodynamic potential (3). The diagram in the vicinity of 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 two-phase region.

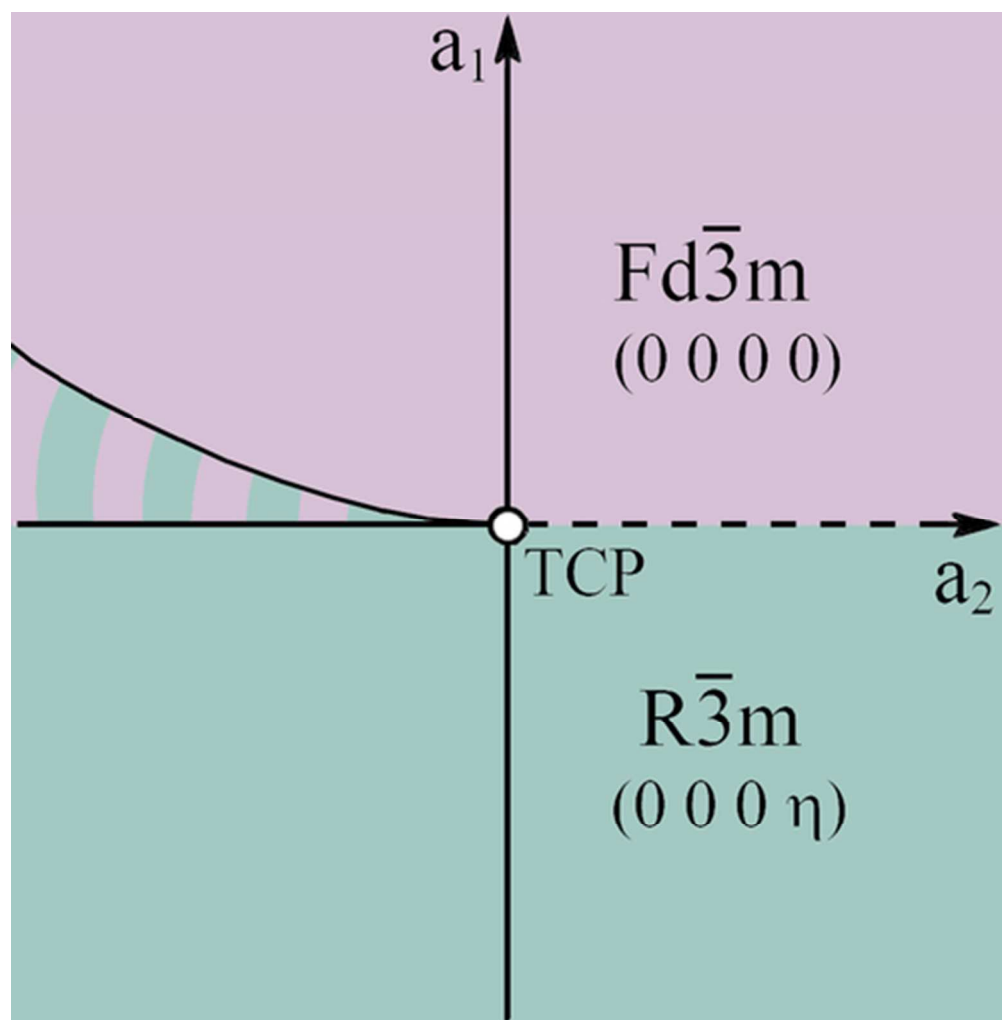
Figure 2. Calculated low-symmetry ordered  $R\bar{3}m$ -spinel structure: atomic presentation (a), polyhedral presentation in the form of  $\text{Cu}(2)[\text{S}(3)_3\text{S}(2)]$  (yellow) and  $\text{Cu}(1)[\text{S}(4)_3\text{S}(1)]$  (green) tetrahedra and  $\text{Ti}(1)[\text{S}(3)_6]$  (dark blue),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

Figure 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 ( $\text{Ti}(1)$ ,  $\text{Ti}(2)$ ,  $\text{Ti}(3)$ ). The Ti-Ti bond lengths are substantially different (they are marked by different colors).

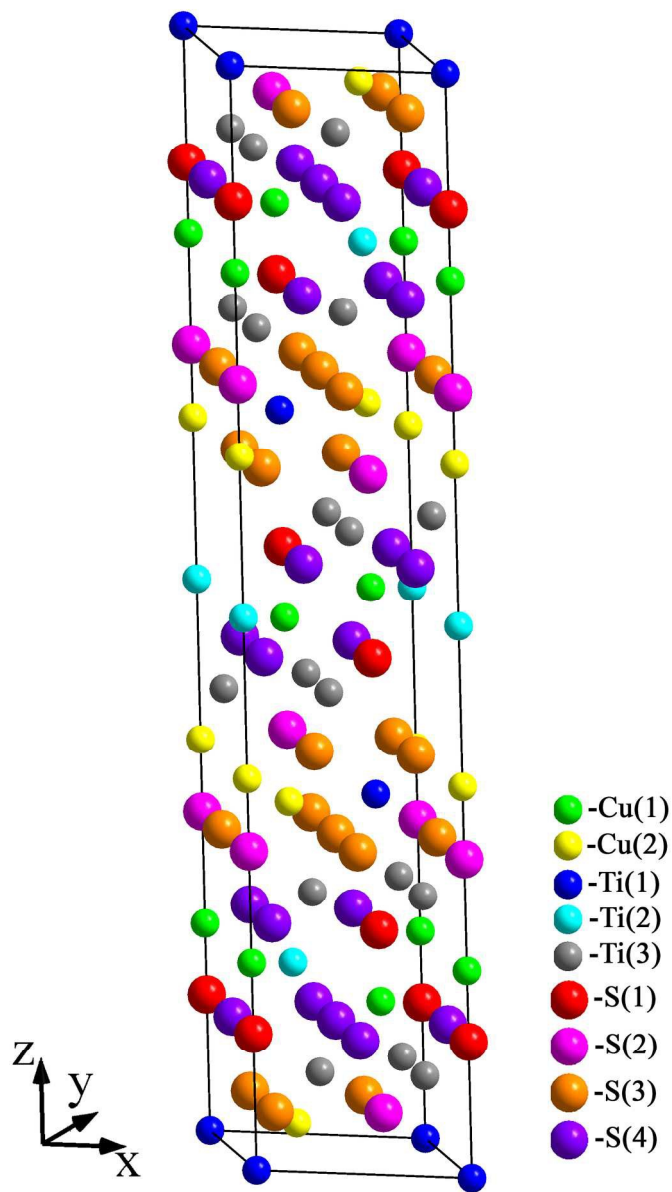
Figure 4. «Bunch» of  $[\text{Cu}(1)\text{-Ti}(3)]$ -dimers.

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 Cu(1)-atom (c).

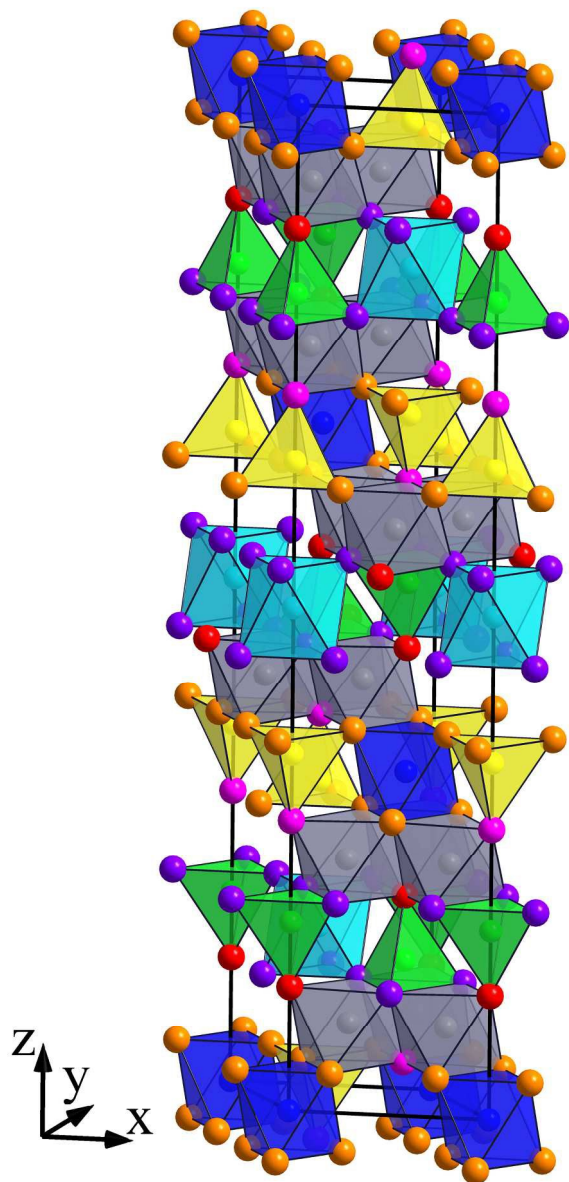
Fig. 6.  $[\text{Ti}(1)\text{Ti}(3)_6]$ - and  $[\text{Ti}(2)\text{S}(4)_6]$ -heptamers in  $\text{CuTi}_2\text{S}_4$  rhombohedral structure.  $[\text{Ti}(1)\text{Ti}(3)_6]$ -heptamers, each of which is made of one Ti(1) (dark blue) and six Ti(3) ions (grey) connected by the shorter Ti-Ti bonds (shown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



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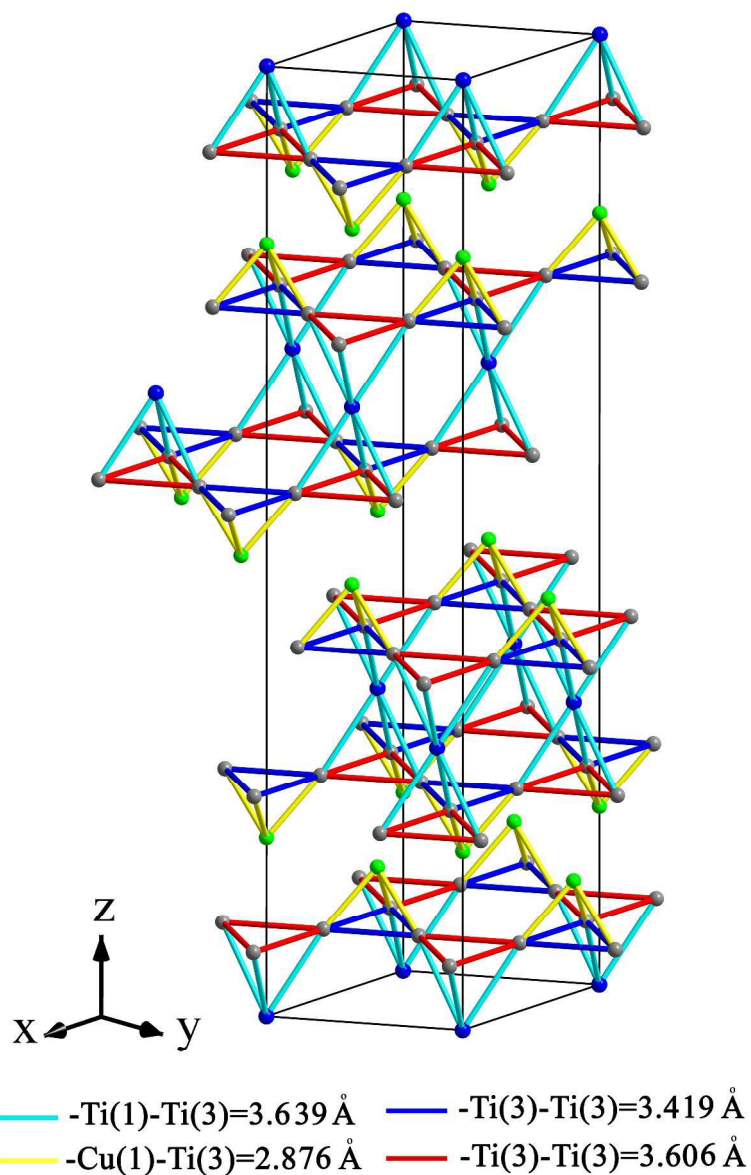


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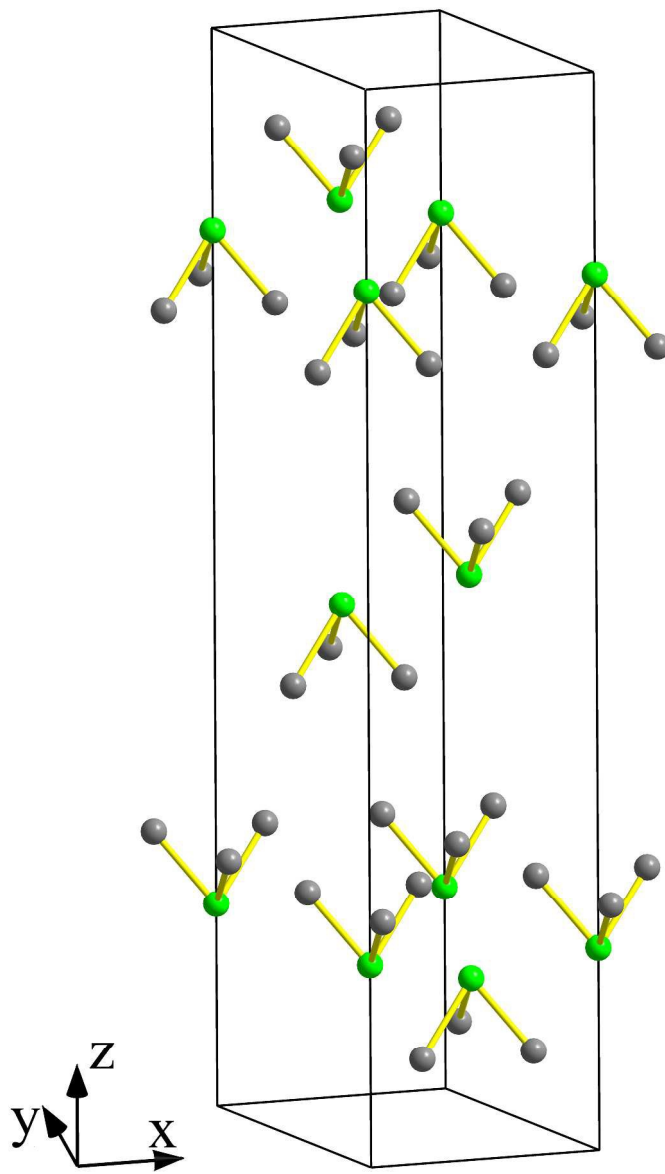


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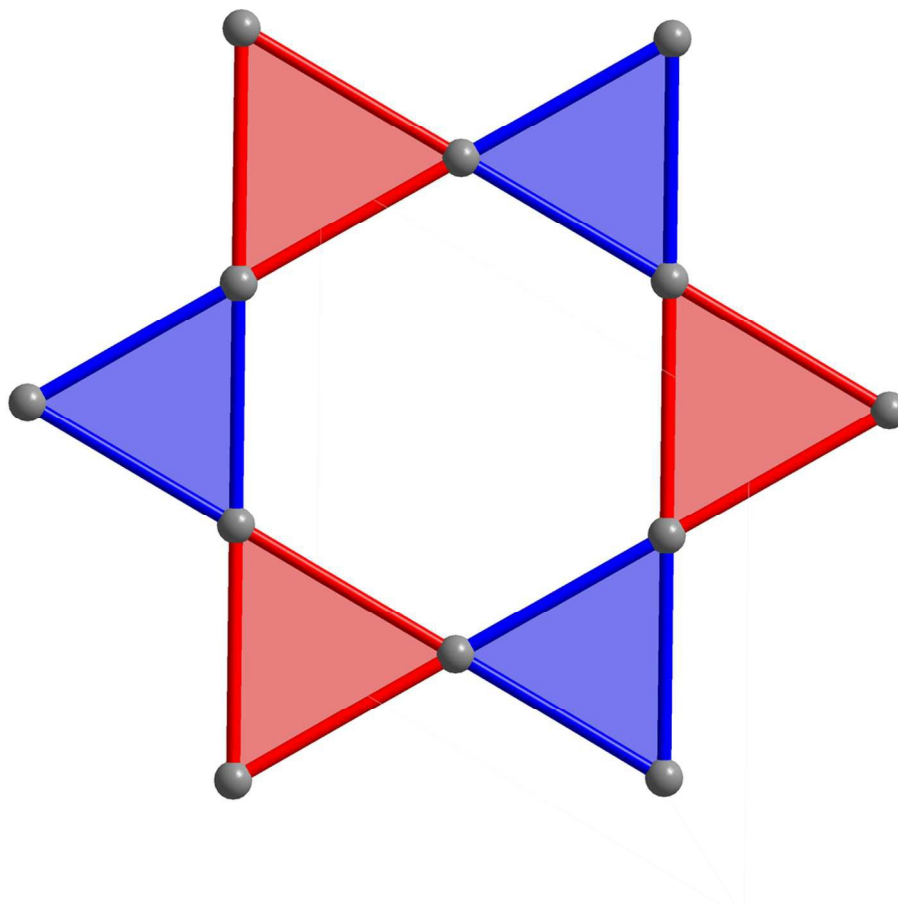




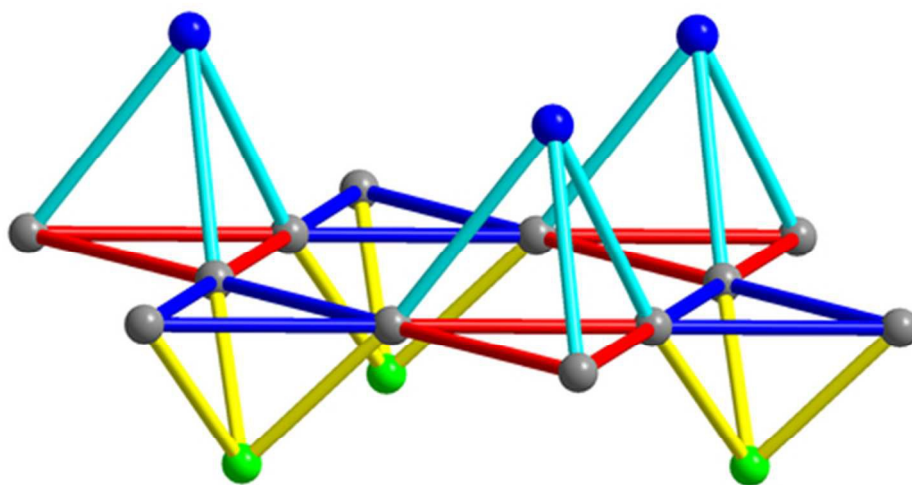
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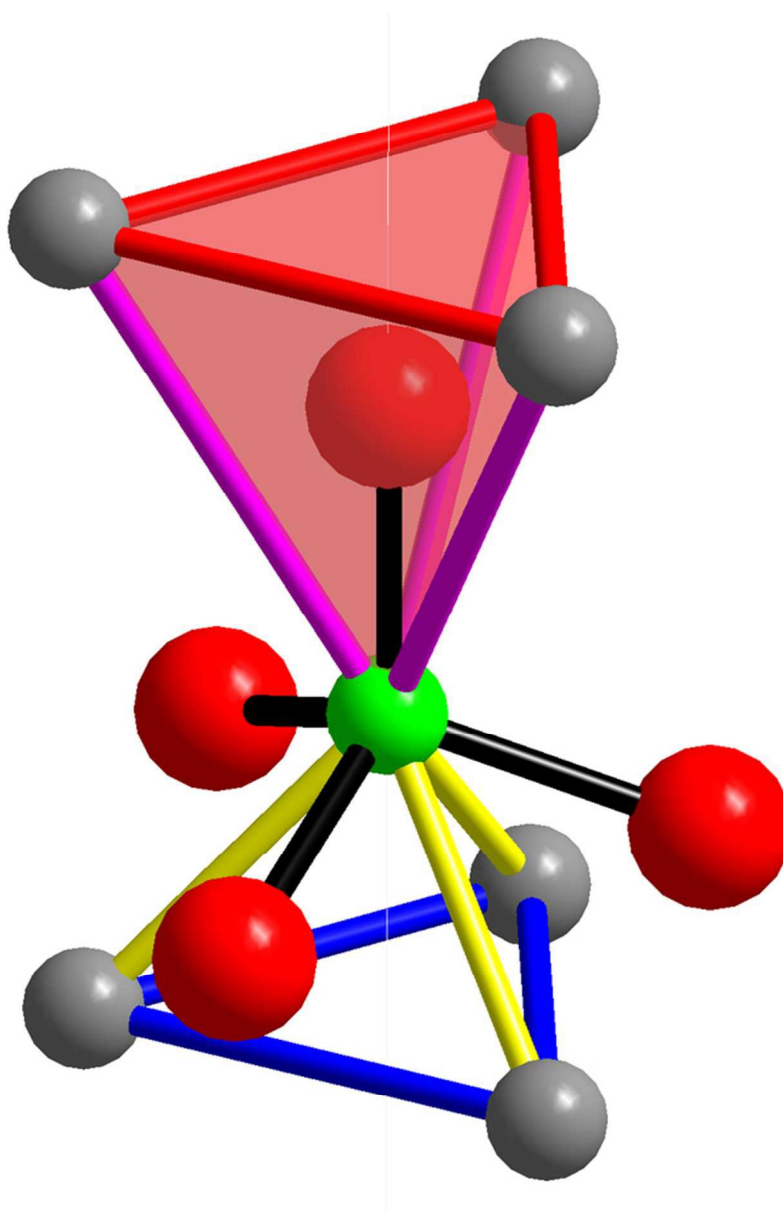
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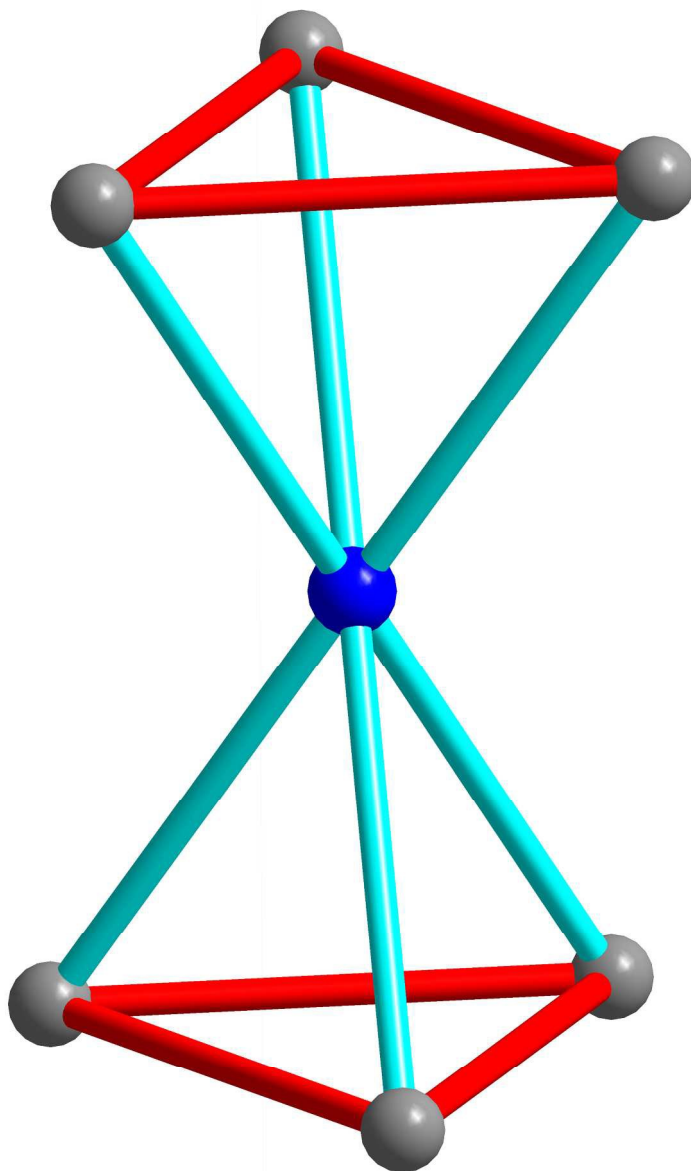
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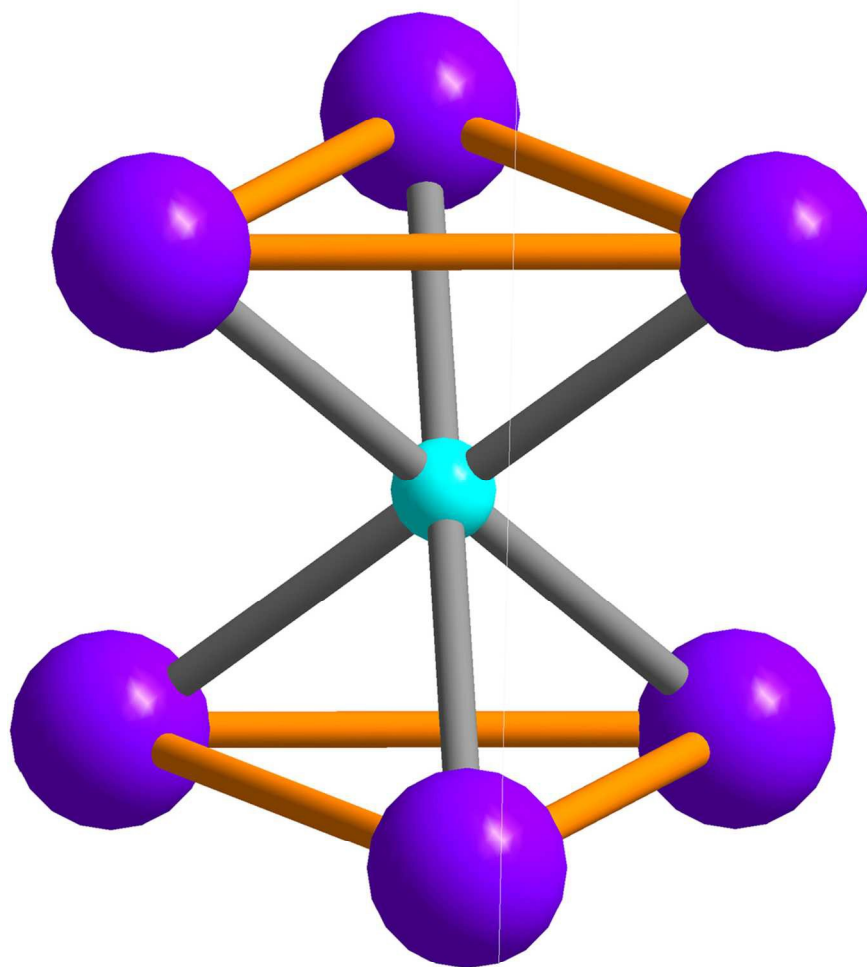
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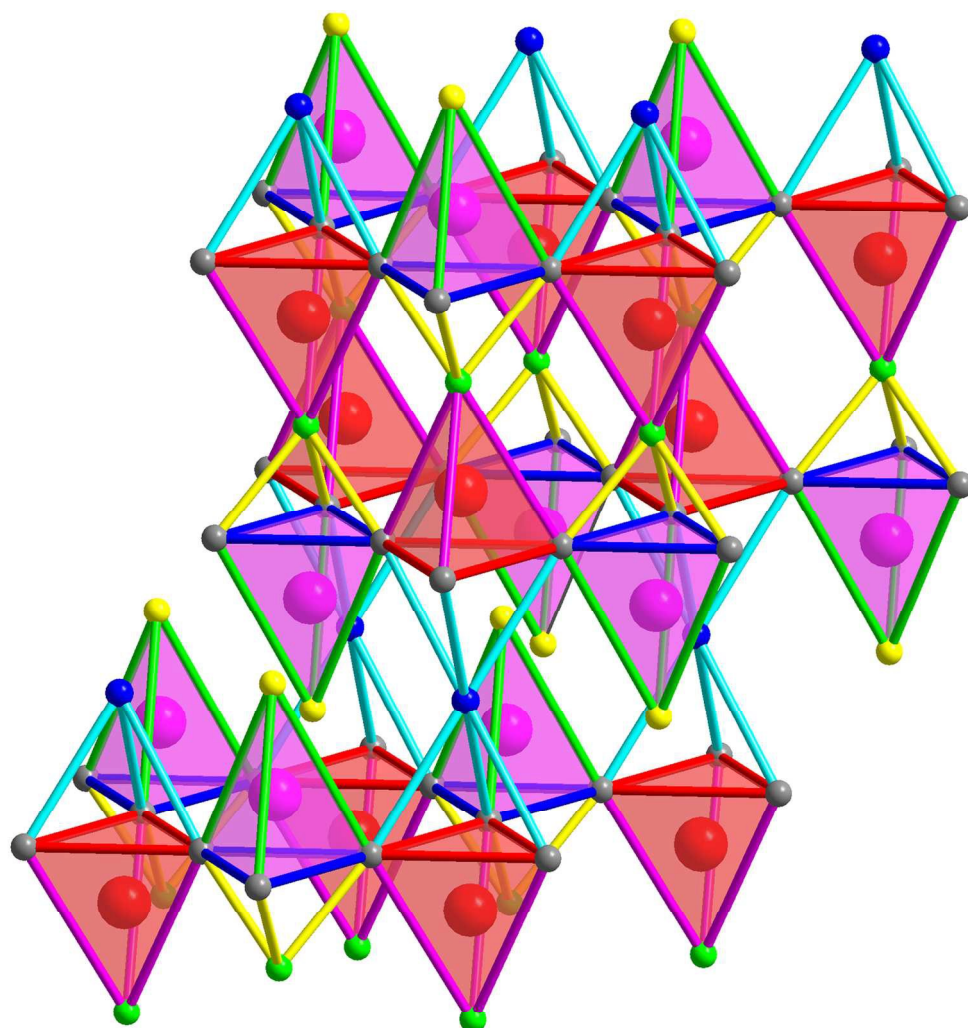
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— - Ti(2)-S(4) = 2.515 Å

— - S(4)-S(4) = 3.376 Å

90x125mm (300 x 300 DPI)

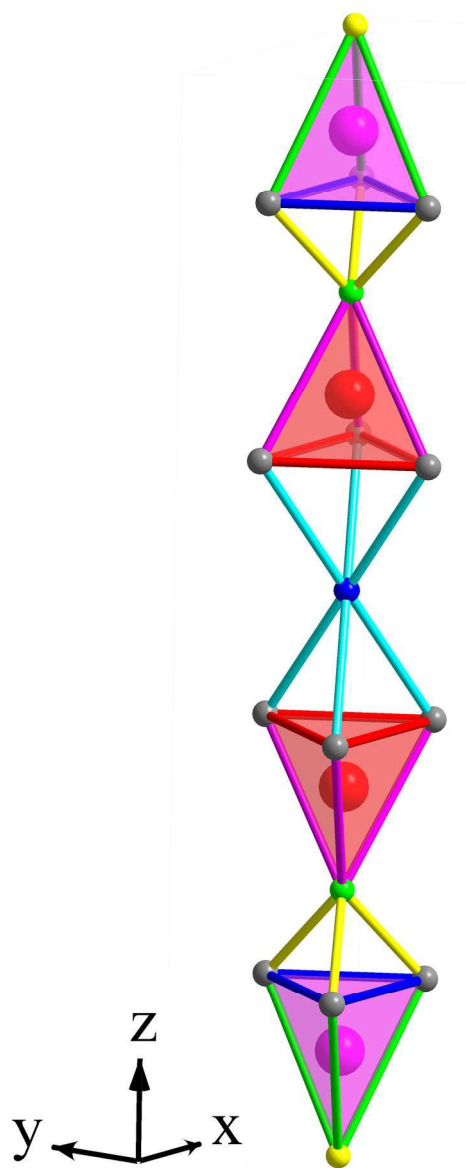


— -Cu(1)-Ti(3)=4.115 Å

— -Cu(2)-Ti(3)=4.209 Å

165x181mm (300 x 300 DPI)





132x340mm (300 x 300 DPI)