Frustrated Antiferromagnetic Spin Chains of Edge-Sharing Tetrahedra in Volcanic Minerals

K₃Cu₃(Fe₀.₈₂Al₀.₁₈)O₂(SO₄)₄ and K₄Cu₄O₂(SO₄)₄MeCl

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Abstract The calculation of the sign and strength of magnetic interactions in two noncentrosymmetric minerals (klyuchevskite, K₃Cu₃(Fe₀.₈₂Al₀.₁₈)O₂(SO₄)₄, and piipite, K₄Cu₄O₂(SO₄)₄Cu₀.₅Cl) has been performed based on the structural data. As seen from the calculation results, both minerals comprise quasi-one-dimensional frustrated antiferromagnets. They contain frustrated spin chains from edge-sharing Cu₄ tetrahedra with strong antiferromagnetic couplings within chains and very weak ones between chains. Strong frustration of magnetic interactions is combined with the presence of the electric polarization in tetrahedral chains in piipite. The uniqueness of magnetic structures of these minerals caused by peculiarities of their crystal structures has been discussed.

Keywords Frustrated quasi-one-dimensional antiferromagnets · Tetrahedral spin chains · Klyuchevskite K₃Cu₃(Fe₀.₈₂Al₀.₁₈)O₂(SO₄)₄ · Piipite K₄Cu₄O₂(SO₄)₄MeCl

1 Introduction

The technological developments put forward new requirements to properties of the applied crystalline materials. In this regard, the potential of crystals of simple chemical compounds is almost exhausted. Here, one of the ways of further development will consist of the selection of materials with required properties from natural objects and creation of novel functional materials on their basis. The objective of the present work was to reveal magnetic materials, which can be of not only scientific but also practical importance, among fumaroles of Tolbachik volcanoes (Kamchatka Peninsula, Russia) [1].

The search and study of compounds with the spin \((S) = 1/2\), whose magnetic subsystem is strongly frustrated, prevents, in some cases, the formation of a long-range order until realization of exotic states such as “spin ice” and “spin liquid” has been constituted one of the key focuses in the physics of the condensed state during the recent 20 years [2–10]. The most active studies were concerned with frustrated magnetics composed of vertex-sharing tetrahedra of magnetic ions. It is well known that this type of the most frustrated magnetic lattice can be found in spinels and compounds of the pyrochlore type. We suggest that minerals of fumaroles of Tolbachik volcanoes can be also strongly frustrated antiferromagnets. The point is that the framework of crystal structures of many of these minerals is formed by anion-centered XM₄ tetrahedra of magnetic ions, for instance \([OCu₄]^{5+}\), linking to each other with formation of isle-like complexes, infinite chains, layers, or frameworks [11–14]. Therefore, the crystal structure of these minerals itself provides the possibility of the emergence of a strongly frustrated magnetic system. The authors from the St. Petersburg School of Structural Mineralogy and Crystal Chemistry determined the crystal structures, studied the crystal chemistry, and performed the systematization of minerals with anion-centered complexes [11–14]. However, unlike structural properties, the magnetic properties of these minerals have been studied very poorly yet.

The objective of the present work was to find genetic basics determined by the crystal structure and...
determining, in its turn, the magnetic structure and properties of two noncentrosymmetric minerals: klyuchevskite (K₃Cu₃(Fe₀.₈₂Al₀.₁₈)O₂(SO₄)₄ [15]) and piipite (K₄Cu₄O₂(SO₄)₄Cu₀.₅Cl [16]). For this purpose, based on the data on crystal structures of these minerals, characteristics (sign and strength) of magnetic interactions were calculated, and their competition was examined. These compounds are characterized with similar geometries of exchange bonds—quasi-one-dimensional chains from edge-sharing copper tetrahedra.

2 Method of Calculation

To determine the characteristics of magnetic interactions (type of the magnetic moment ordering and strength of magnetic coupling) in minerals K₃Cu₃(Fe₀.₈₂Al₀.₁₈)O₂(SO₄)₄ and K₄Cu₄O₂(SO₄)₄MeCl, we used the earlier developed phenomenological method (named the “crystal chemistry method”) and the program “MagInter” created on its basis [17–21]. In this method, three well-known concepts about the nature of magnetic interactions are used. Firstly, according to Kramers’s idea [22], in exchange couplings between magnetic ions separated by one or several diamagnetic groups, the electrons of nonmagnetic ions play a considerable role. Secondly, in the Goodenough–Kanamori–Anderson model [23–26], the crystal chemical aspect points clearly to the dependence of strength interaction and the type of orientation of spins of magnetic ions on the arrangement intermediate anions. Thirdly, as in the polar Vonsovsky model [27], by consideration of magnetic interactions, we took into account not only anions, which are valent bound with the magnetic ions, but also all the intermediate negatively or positively ionized atoms, with the exception of cations of metals with no unpaired electrons.

The method enables one to determine the sign (type) and strength of magnetic couplings on the basis of structural data. According to this method, the coupling between magnetic ions Mᵢ and Mⱼ emerges in the moment of crossing the boundary between them by an intermediate ion (Aₙ) with the overlapping value of ~ 0.1 Å. The area of the limited space (local space) between the Mᵢ and Mⱼ ions along the bond line is defined as a cylinder, whose radius is equal to these ion radii. The strength of magnetic couplings and the type of magnetic moment ordering in insulators are determined mainly by the geometrical position and the size of intermediate Aₙ ions in the local space between the two magnetic ions (Mᵢ and Mⱼ). The positions of intermediate ions (Aₙ) in the local space are determined by the distance h(Aₙ) from the center of the ion Aₙ up to the bond line Mᵢ–Mⱼ and the degree of the ion displacement to one of the magnetic ions expressed as a ratio (lᵣ/₀/lₙ) of the lengths lᵣ and lₙ (lᵣ ≤ lₙ; lᵣ = d(Mᵢ–Mⱼ)–lₙ) produced by the bond line Mᵢ–Mⱼ division by a perpendicular made from the ion center (Fig. 1).

The intermediate Aₙ ions will tend to orient the magnetic moments of Mᵢ and Mⱼ ions and make their contributions (jₙ) into the emergence of antiferromagnetic (AFM) or ferromagnetic (FM) components of the magnetic interaction in dependence on the degree of overlapping of the local space between magnetic ions (Δh(Aₙ)), the asymmetry (lᵣ/₀/lₙ) of position relative to the middle of the Mᵢ–Mⱼ bond line, and the distance between magnetic ions (Mᵢ–Mⱼ).

Among the above parameters, only the degree of space overlapping between the magnetic ions Mᵢ and Mⱼ (Δh(Aₙ) = h(Aₙ) – rₐₙ) equal to the difference between the distance h(Aₙ) from the center of Aₙ ion up to the bond line Mᵢ–Mⱼ and the radius (rₐₙ) of the Aₙ ion determined the sign of magnetic interaction. If Δh(Aₙ) < 0, the Aₙ ion overlaps (by —Δh—) the bond line Mᵢ–Mⱼ and initiates the emerging contribution into the AFM component of magnetic interaction. If Δh(Aₙ) > 0, there remains a gap (the gap width Δh) between the bond line and the Aₙ ion, and this ion initiates a contribution to the FM component of magnetic interaction.

The sign and strength of the magnetic coupling (Jₖ) are determined by the sum of the above contributions:

\[ J_{ij} = \sum_{n} J_{n} \]
The value $J_{ij}$ is expressed in per angstrom units. If $J_{ij} < 0$, the type of $M_i$ and $M_j$ ion magnetic ordering is AFM, and in opposite, if $J_{ij} > 0$, the ordering type is FM.

The method is sensitive to insignificant changes in the local space of magnetic ions and enables one to find intermediate ions localized in critical positions, and deviations from which would result in the change of the magnetic coupling strength or spin reorientation (AFM-to-FM transition, for instance, under the effect of temperature or external magnetic field).

The format of the initial data for the MagInter program (crystallographic parameters, atom coordinates) is in compliance with the cif file in the Inorganic Crystal Structure Database (ICSD) (FIZ, Karlsruhe, Germany). The room-temperature structural data and ionic radii of Shannon [28] were used for calculations.

The comparison of our data with that of other methods shows that the scaling factors ($K$) for translating the value in per angstrom into kelvin in oxides $Cu_2O$, $Fe_3O_4$, and $Cu_3Fe$ are equal to 6591, 399, and 511, respectively (Table 1). Energy converter is $1 \text{ K} = 0.0862 \text{ meV}$.

Studies of the minerals of interest were performed in the following order:

- The sign and strength of all the magnetic interactions between magnetic ions as inside low-dimensional fragments of the sublattice of magnetic ions as between them were calculated.
- The probability of the emergence of anomalies of magnetic interactions and magnetic phase transitions in case of insignificant changes in the local space between magnetic ions was determined.
- The specific geometric configurations in sublattices of magnetic ions, in which the competition of magnetic interactions takes place, were identified.
- The conclusions on these compound magnetic structures were made based on the obtained data on the characteristics of magnetic interactions and the presence of geometric frustrations in these interactions.

Tables 2 and 3 (Section 3) show the crystallographic characteristics and parameters of magnetic couplings ($J_{in}$) calculated on the basis of structural data and respective distances between magnetic ions in the materials under study. Besides, for intermediate X ions providing the maximal contributions ($J^{\text{max}}$) into AFM or FM components of these $J_{in}$ couplings, the degree of overlapping of the local space between magnetic ions ($\Delta h(X)$), the asymmetry ($l_p/l_n$) of the position relative to the middle of the $M_i$–$M_j$ bond line, and the $M_i$–X–$M_j$ angle are presented.

3 Results and Discussion

3.1 Klyuchevskite, $K_3Cu_3(Fe_{0.82}Al_{0.18})O_2(SO_4)_4$

Klyuchevskite ($K_3Cu_3(Fe_{0.82}Al_{0.18})O_2(SO_4)_4$) [15] crystallizes in the noncentrosymmetric monoclinic $I2$ system. Magnetic $Cu^{2+}$ ions occupy three crystallographically independent sites $Cu_1$, $Cu_2$, and $Cu_3$ and have a characteristic distortion of $Cu^{2+}$ coordination polyhedra due to the Jahn–Teller effect strengthened by geometric hindrances related to the packing features. Elongated tetragonal pyramids ($CuO_5$) with a strong shift of copper ions to basal planes serve as the coordination surrounding $Cu_1$, $Cu_2$, and $Cu_3$. As a result, the $Cu$–O distances to apical pyramidal vertices ($Cu_1$–$O11 = 2.54 \text{ Å}$, $Cu_2$–$O12 = 2.47 \text{ Å}$, and $Cu_3$–$O8 = 2.86 \text{ Å}$) are significantly longer than to basal vertices (1.70–2.05 Å). The $Cu$–O distances to the sixth oxygen atom exceed 2.95 Å for all copper ions. The $Fe^{3+}$ ions occupy the only crystallographically independent site ($Fe1$) and have the octahedral surrounding ($Fe1$–$O = 1.78–2.07 \text{ Å}$) with an insignificant distortion, as compared to the $Cu^{2+}$ coordination. According to Ref. [15], in this klyuchevskite sample, 18 % of $Fe^{3+}$ ions are substituted by nonmagnetic $Al^{3+}$ ions. However, we consider its crystal structure as a model, in which the $Fe1$ position is fully occupied by magnetic $Fe^{3+}$ ions, and assume that such a compound can be synthesized.

The characteristic feature of this structure, as of a majority of crystal structures of minerals from volcanic exhalations of Kamchatka (Russia) [11–15], consists in the presence of complexes of anion-centered OMe$_4$ tetrahedra (Fig. 2a, b). “Extra” oxygen anions ($O17$ and $O18$) and “pullover” magnetic cations form two types of oxo-centered tetrahedra: [O17Cu1Cu2Cu3Fe] ($O17$–Cu = 1.91–1.97 Å; $O17$–Fe = 1.85 Å) and [O18Cu1Cu2Cu3Fe] ($O18$–Cu = 1.79–1.90 Å; $O18$–Fe = 2.07 Å) with comparatively high strengths of chemical bonds. Let us denote the tetrahedra centered with the $O17$ ion as type I and the $O18$-centered ones as type II. These oxo-centered [Cu$_3$Fe] tetrahedra are linked through edges ($Cu_1$–$Cu_2 = 2.899 \text{ Å}$ and $Cu_3$–$Fe = 2.918 \text{ Å}$) into chains stretched along the $b$ axis. The chains are linked to each other through $SO_4$ tetrahedra and $K$ ions. The chains of edge-sharing $Cu_1Cu_2Cu_3Fe$ tetrahedra serve as a base of the sublattice of magnetic ions (Fig. 2b, d) in klyuchevskite. Tetrahedra of I and II types alternate in the chain.

Our calculations (Table 2, Fig. 2b, d) demonstrate that strong AFM couplings exist along all the $Cu$–$Cu$ tetrahedral edges, except one ($Cu_2$–$Cu_3$ in the tetrahedron of type I). The main contribution to the formation of the AFM character of these couplings is provided by $O18$ and $O17$ oxygen ions centering the above tetrahedra. The AFM $J_{1}$
Table 1 An estimate of $J_n$ magnetic couplings in oxides Cu$^{2+}$, Fe$^{3+}$, and Cu$^{2+}$–Fe$^{3+}$ by a crystal chemical method (I) and experimental and quantum-chemical methods (II)

| Compounds                  | Space group, lattice parameters | $d$(M–M) (Å) | $|J| (\text{Å}^{-1})$ | $J_c$ (degree Kelvin) | $K^{(a)}$ | $K^2 \times J$ (Å$^{-1}$) (degree Kelvin) |
|----------------------------|---------------------------------|--------------|----------------------|------------------------|----------|------------------------------------------|
| AgCuVO$_4$, 293 K [29]     | $Pnma$ (no. 62): $a = 9.255, b = 6.778, c = 5.401$ Å, $Z = 4$ | $d$(Cu–Cu) = 3.389 | 0.0474 (AFM) | 330 (AFM) [30] | 6591 | 312 (AFM) |
| ICSD no. 419201            |                                 |              |                      |                        |          |                                          |
| AgCuVO$_4$, 120 K [29]     | $Pnma$ (no. 62): $a = 9.242, b = 6.775, c = 5.396$ Å, $Z = 4$ | $d$(Cu–Cu) = 3.388 | 0.0483 (AFM) | 330 (AFM) [30] | 6591 | 318 (AFM) |
| ICSD no. 419202            |                                 |              |                      |                        |          |                                          |
| BaCu$_2$Ge$_2$O$_7$ [31]   | $Pnma$ (no. 62): $a = 7.048, b = 13.407, c = 5.401$ Å, $Z = 4$ | $d$(Cu–Cu) = 3.546 | 0.0864 (AFM) | 540 (AFM) [32, 33] | 6591 | 569 (AFM) |
| ICSD no. 51282             |                                 |              |                      |                        |          |                                          |
| Cu$_3$(AsO$_4$)(OH)$_3$ [34]| $P2_1/c$ (no. 14): $a = 7.257, b = 6.457, c = 12.378$ Å $\beta = 99.51^\circ$, $Z = 4$ | $d$(Cu–Cu) = 3.131 | 0.0532 (AFM) | 300 (AFM) [35] | 6591 | 351 (AFM) |
| ICSD no. 68456             |                                 |              |                      |                        |          |                                          |
| Cu$_2$Te$_2$O$_5$Cl [36]   | $P\bar{1}$ (no. 81): $a = 9.242, b = 6.775, c = 5.396$ Å, $Z = 4$ | $d$(Cu–Cu) = 3.230 | 0.0117 (AFM) | 38.5 (AFM) [36] | 6591/2 | 38.6 (AFM) |
| ICSD no. 89978             |                                 |              |                      |                        |          |                                          |
| Cu$_2$Fe$_2$Ge$_2$O$_7$ [38]| $P2_1/m$ (no. 11): $a = 7.315, b = 17.224$ Å, $\gamma = 120^\circ$, $Z = 3$ | $d$(Fe–Fe) = 3.658 | 0.0947 (AFM) | 37 (AFM) [43] | 399 | 37.8 (AFM) |
| ICSD no. 204015            |                                 |              |                      |                        |          |                                          |
| FeTe$_2$O$_5$Cl [46]       | $P2_1/c$ (no. 14): $a = 13.153, b = 6.595, c = 14.145$ Å $\beta = 108.77^\circ$, $Z = 8$ | $d$(Fe–Fe) = 3.151 | 0.0330 (AFM) | 10.2 (AFM) [46] | 399 | 13.2 (AFM) |
| ICSD no. 204092            |                                 |              |                      |                        |          |                                          |
| FeTe$_2$O$_5$Br [46]       | $P2_1/c$ (no. 14): $a = 13.153, b = 6.595, c = 14.145$ Å $\beta = 108.77^\circ$, $Z = 8$ | $d$(Fe–Fe) = 3.159 | 0.0361 (AFM) | 11.7 (AFM) [46] | 399 | 14.4 (AFM) |
| ICSD no. 204090            |                                 |              |                      |                        |          |                                          |
| K$_4$Cu$_2$O$_2$(SO$_4$)$_4$Cu$_3$Cl [16]| $I4$ (no. 79): $a = 13.60$ Å, $c = 4.98$ Å, $Z = 2$ | $d$(Cu–Cu) = 2.936 | 0.0719 (AFM) | 6591/2 | 237 (AFM) |
| ICSD no. 64684             |                                 |              |                      |                        |          |                                          |
| K$_3$Cu$_8$(Fe$_{0.82}$Al$_{0.18}$)O$_2$(SO$_4$)$_4$ [15]| $I2$ (no. 5): Tetrahedron | $d$(Cu–Cu) = 3.220 | 0.0986 (AFM) | 6591 | 650 (AFM) |
| ICSD no. 67698             |                                 |              |                      |                        |          |                                          |
| Compounds | Space group, lattice parameters | $d_M$ (Å) | $J$ (degree Kelvin) | $K$ (degree Kelvin) |
|-----------|---------------------------------|-----------|--------------------|--------------------|
| Tetrahedron II | $d_{Cu-Cu} = 3.331$ | 4.940 | 473.91 (AFM) | $K$ (Å$^{-1}$) |
| | $d_{Cu-Cu} = 3.115$ | 51.11 | 305.2 b (AFM) | $J$ (degree Kelvin) |
| | $d_{Fe-Cu} = 3.268$ | 40.95 b (AFM) | 275.91 (AFM) | $I$ (This work) |
| | $d_{Fe-Cu} = 3.193$ | 39.9 b (AFM) | 275.91 (AFM) | $J$ (degree Kelvin) |
| | $d_{Fe-Fe} = 4.940$ | 4.940 | 473.91 (AFM) | $K$ (degree Kelvin) |
| | $d_{Fe-Fe} = 3.193$ | 39.9 b (AFM) | 275.91 (AFM) | $J$ (degree Kelvin) |

$J_1 = -0.0986$ Å$^{-1}$, $d(Cu1–Cu3) = 3.220$ Å) coupling is the strongest among them. The antiferromagnetic $J_1, J_5$ ($d(Fe–Cu1) = 3.400$ Å) and $J_6$ ($d(Fe–Cu2) = 3.364$ Å) couplings in the tetrahedron of type I and antiferromagnetic $J_7$ ($d(Cu1–Cu3) = 3.331$ Å), $J_8$ ($d(Cu2–Cu3) = 3.115$ Å), $J_9$ ($d(Fe–Cu2) = 3.268$ Å), and $J_{10}$ ($d(Fe–Cu1) = 3.193$ Å) couplings in the tetrahedron of type II emerge under the effect of $O_{18}$ and $O_{17}$ ions, respectively. The contributions to AFM components of interactions $J_2$ ($d(Cu1–Cu2) = 2.899$ Å) and $J_4$ ($d(Fe–Cu3) = 2.918$ Å) along common tetrahedral edges in the chain are provided by both $O_{17}$ and $O_{18}$ ions.

The $J_3$ coupling ($d(Cu2–Cu3) = 2.870$ Å) between magnetic Cu2 and Cu3 ions in the tetrahedron of type I is formed under the effect of two oxygen ions ($O_{18}$ and $O_{12}$) entering its local space. Although the oxygen $O_{18}$ ion makes a substantial AFM contribution ($j(O_{18}) = -0.0604$ Å$^{-1}$) to the emergence of the $J_3$ coupling, the FM contribution of the $O_{12}$ ion ($j(O_{12}) = 0.0632$ Å$^{-1}$) exceeds it insignificantly (by 0.0028 Å$^{-1}$) and, thus, makes this coupling weak ferromagnetic. Then, along the zigzag-like chain formed by Cu2–Cu3 tetrahedral edges, the orientation of magnetic moments will be as follows: $\uparrow \uparrow \downarrow \downarrow$. Nevertheless, the $J_3$ coupling can be hardly considered as a stable one. The point is the $O_{12}$ ion is located in the critical position, and a shift from it could result in reorientation of magnetic moments (FM-to-AFM transition). For example, the decrease of the Cu2–O12 distance from 2.47 to 2.34 Å (at the increase of the values of $x$ and $z$ coordinates of the $O_{12}$ ion by just 0.01) will yield fivefold decrease of the FM contribution and induce the transition of the $J_3$ coupling into the AFM state. Low accuracy of determination of the crystal structure of klyuchevskite in Ref. [15] by means of X-ray single-crystal diffraction (the refinement converged to the residual factor ($R$) values $R = 0.12$) enables one to assume that the $O_{12}$ ion has an insignificant role in the formation of the $J_3$ coupling, so that it is strong and antiferromagnetic ($J_3/J_1 = 0.61$), just like the other couplings in tetrahedra.

To sum up, the crystal structure of klyuchevskite causes the emergence of strongly frustrated AFM chains of edge-sharing tetrahedra stretched along the $b$ axis, with competing strong nearest neighbor AFM couplings along the tetrahedral edges. In case of reorientation of magnetic moments from antiferromagnetic to ferromagnetic (AFM $J_3 \rightarrow$ FM $J_3$) along just one of six tetrahedron edges, all the magnetic couplings in the tetrahedron will remain frustrated. In case of complete substitution of $Fe^{3+}$ ions by nonmagnetic $Al^{3+}$ ions at preservation of the crystal structure, the frustrated AFM chain from tetrahedra will transform into a corrugated AFM chain from copper triangles alternately coupled through a side and a vertex (Fig. 2c). This chain will be also frustrated.
Crystallographic characteristics and parameters of magnetic couplings ($J_n$) calculated on the basis of structural data and respective distances between magnetic ions in klyuchevskite $K_3Cu_3(Fe_{0.82}Al_{0.18})O_2(SO_4)_4$.

$K_3Cu_3(Fe_{0.82}Al_{0.18})O_2(SO_4)_4$ [15] (data for ICSD no. 67698)

Space group I2 (N5): $a = 18.667$ Å, $b = 4.94$ Å, $c = 18.405$ Å, $\alpha = 90^\circ$, $\beta = 101.5^\circ$, $\gamma = 90^\circ$, $Z =$

Method$^a$-XDS; $R$-value$^b = 0.12$

| | $J_n$ ($\text{Å}^{-1}$) | $j_{\text{max}}$ ($\text{Å}^{-1}$) | | | $J_n$ ($\text{Å}^{-1}$) | $j_{\text{max}}$ ($\text{Å}^{-1}$) |
|---|---|---|---|---|---|---|
| | ($\Delta h(X)$, $U_m^f$, $M_i$–$X$–$M_j$) | ($\Delta h(X)$, $U_m^f$, $M_i$–$X$–$M_j$) | | | ($\Delta h(X)$, $U_m^f$, $M_i$–$X$–$M_j$) | ($\Delta h(X)$, $U_m^f$, $M_i$–$X$–$M_j$) |
| **tetrahedron I:** O18Cu1Cu2Cu3Fe$^b$ | | | | | | |
| d(Cu1–Cu3) | $J_1$ | $j$(O18): −0.0986 | d(Fe–Cu3) | $J_4$ | $j$(O18): −0.0400 |
| 3.220 | −0.0986 | (−0.509, 1.8, 122.04$^\circ$) | 2.918 | −0.0761 | (−0.169, 1.12, 99.6$^\circ$) |
| d(Cu1–Cu2) | $J_2$ | $j$(O18): −0.0331 | d(Fe–Cu1) | $J_5$ | $j$(O18): −0.0361 |
| 2.899 | −0.0756 | (−0.139, 1.01, 97.96$^\circ$) | 3.400 | −0.0671 | (−0.149, 1.29, 98.3$^\circ$) |
| d(Cu2–Cu3) | $J_3$ | $j$(O18): −0.0604 | d(Fe–Cu2) | $J_6$ | $j$(O18): −0.0629 |
| 2.870 | −0.0604 | (−0.248, 1.10, 102.38$^\circ$) | 3.364 | −0.0515 | (−0.353, 1.13, 116.1$^\circ$) |
| (0.0028) | | (0.216, 1.88, 80.89$^\circ$) | | | |
| **tetrahedron II:** O17Cu1Cu2Cu3Fe$^b$ | | | | | | |
| d(Cu1–Cu3) | $J_7$ | $j$(O17): −0.0719 | d(Fe–Cu2) | $J_9$ | $j$(O17): −0.0854 |
| 3.331 | −0.0719 | (−0.399, 1.04, 118.0$^\circ$) | 3.268 | −0.0854 | (−0.455, 1.06, 119.8$^\circ$) |
| d(Cu2–Cu3) | $J_8$ | $j$(O17): −0.0463 | d(Fe–Cu1) | $J_{10}$ | $j$(O17): |
| 3.115 | −0.0463 | (−0.224, 1.04, 105.9$^\circ$) | 3.193 | −0.0801 | (−0.408, 1.05, 116.24$^\circ$) |
| **intrachain couplings:**$^b$ | | | | | | |
| d(Cu1–Cu1) | $J_{b1}^{\text{Cu1}}$ | $j$(O2): −0.0193 | d(Cu1–Cu2) | $J_{11}$ | $j$(O17): |
| 4.940 | 0.0227 | (−0.189, 1.99, 123.5$^\circ$) | 5.664 | −0.0208 | (−0.730, 2.16, 153.1$^\circ$) |
| | | (0.480, 1.09, 105.4$^\circ$) | $j$(O4): 0.0395 | | $j$(O18): |
| d(Cu2–Cu2) | $J_{b2}^{\text{Cu2}}$ | $j$(O5): 0.0240 | d(Cu1–Cu2) | $J_{12}$ | $j$(O17): |
| 4.940 | 0.0276 | (0.292, 1.03, 111.2$^\circ$) | 5.791 | −0.0213 | (152.3$^\circ$) |
| | | (152.3$^\circ$) | | | |
| d(Cu3–Cu3) | $J_{b3}^{\text{Cu3}}$ | $j$(O12): −0.0047 | d(Fe–Cu3) | $J_{13}$ | $j$(O17): |
| 4.940 | −0.0042 | (−0.258, 2.26, 124.6$^\circ$) | 5.552 | −0.0221 | (−0.732, 2.23, 148.9$^\circ$) |
| | | | | | |

$^a$ Method: X-ray diffraction

$^b$ $R$-value: 0.12
Table 2 (continued)

K$_3$Cu$_3$(Fe$_{0.82}$Al$_{0.18}$)O$_2$(SO$_4$)$_4$[15] (data for ICSD no. 67698)

Space group $I2$ (N5); $a = 18.667$ Å, $b = 4.94$ Å, $c = 18.405$ Å, $\alpha = 90^\circ$, $\beta = 101.5^\circ$, $\gamma = 90^\circ$, $Z =$

Method$^a$–XDS; R–value$^b$ = 0.12

| d(Fe−Fe) | $J^b_{Fe}$ | $j$(O16): −0.0095 | d(Fe−Cu3) | $J^{14}$ | $j$(O17): −0.0104 |
|----------------|----------|------------------|-----------|----------|------------------|
| 4.940          | −0.0025  | (−0.510, 2.20, 135.4$^\circ$) | 5.918     | −0.0200  | (−0.782, 2.16, 153.1$^\circ$) |

interchain couplings$^b$

| d(Cu2−Cu2) | $J^{15}$ | $j$(O8): −0.0063 | d(Cu3−Cu3) | $J^{18}$ | $j$(O8): −0.0109 |
|--------------|----------|------------------|-----------|----------|------------------|
| 6.333        | −0.0073  | (−0.795, 2.98, 174.3$^\circ$) | 7.722     | −0.0104  | (−0.265, 1.95, 144.0$^\circ$) |

| d(Cu2−Cu3) | $J^{16}$ | $j$(O8): −0.0018 | d(Fe−Cu1) | $J^{19}$ | $j$(O4): −0.0027 |
|-------------|----------|------------------|-----------|----------|------------------|
| 6.399       | −0.0018  | (−0.293, 3.95, 127.2$^\circ$) | 7.947     | −0.0034  | (−0.601, 3.49, 148.3$^\circ$) |

| d(Cu1−Cu1) | $J^{17}$ | $2 \times j$(O11): −0.0017 | d(Cu1−Cu2) | $J^{20}$ | $j$(O11): −0.0332 |
|-------------|----------|------------------|-----------|----------|------------------|
| 6.805       | −0.0006  | (−0.159, 2.07, 135.6$^\circ$) | 8.567     | −0.0300  | (−1.188, 1.25, 174.2$^\circ$) |

$^a$XDS-X-ray diffraction from single crystal
$^b$The refinement converged to the residual factor ($R$) values.
$^c$Jn < 0 - AFM, Jn > 0 - FM
$^d$j-maximal contributions of the intermediate X ion into the AFM component of the Jn coupling
$^e$Δh(X)–the degree of overlapping of the local space between magnetic ions by the intermediate ion X
$^f$l$_n$/l$_m$ is the asymmetry of position of the intermediate X ion relative to the middle of the M$_i$–M$_j$ bond line
$^g$M$_i$–X–M$_j$ bonding angle
$^h$As accepted for Jn calculations, the Fe position is fully occupied
|                | $d$ (Å) | $J_n$ (Å$^{-1}$) | $J_{\text{max}(\delta)}$ (Å$^{-1}$) | $d$ (Å) | $J_n$ (Å$^{-1}$) | $J_{\text{max}(\delta)}$ (Å$^{-1}$) |
|----------------|--------|-----------------|-----------------------------------|--------|-----------------|-----------------------------------|
| $J_{\text{Cu}}$ |        |                 | $\Delta h(X)^\delta$ (Å), $l_n/\ell_l$, Cu-X-Cu$^\delta$ |         |                 | $\Delta h(X)^\delta$ (Å), $l_n/\ell_l$, Cu-X-Cu$^\delta$ |
| $d$(Cu$_1$–Cu$_1$) | 2.936  | $-0.0719$       | $(0.191, 1.0, 101.04^\circ)$       | 3.242  | $-0.0689$       | $(0.362, 1.03, 114.71^\circ)$     |
| Intrachain couplings in tetrahedral chains |         |                 | $j(O1)$: $-0.0443$ |         |                 | $j(O1)$: $-0.0689$ |
| $d$(Cu$_1$–Cu$_1$) | 5.781  | $-0.0211$       | $(0.750, 2.23, 150.75^\circ)$      | 4.980  | $-0.0040$       | $(0.232, 2.21, 101.97^\circ)$     |
| $j(O1)$: $-0.0111$ |         |                 | $(0.111, 2.13, 152.75^\circ)$      |         |                 | $(0.1011, 1.0, 97.79^\circ)$     |
| $d$(Cu$_1$–Cu$_1$) | 7.753  | $-0.0117$       | $(h = -0.362, 1.02, 150.02^\circ)$ | 9.960  | $-0.0051$       | $(0.650, 1.0, 180^\circ)$         |
| Interchain couplings |         |                 | $j(O3)$: $-0.0023$ |         |                 | $j(O3)$: $-0.0126$ |
| $d$(Cu$_1$–Cu$_1$) | 7.240  | $-0.0011$       | $(0.363, 3.04, 139.2)$             | 8.716  | $0.0038$        | $(0.422, 1.68, 153.12^\circ)$     |
| $j(O4)$: $0.0020$ |         |                 | $(0.462, 4.42, 108.2)$             |         |                 | $(0.650, 1.0, 180^\circ)$         |
| Linear chains of Cu$_2$ ions* |         |                 | $j(J_1)$: $0.0140$ |         |                 | $(0.494, 1.13, 132.90^\circ)$     |
| $d$(Cu$_2$–Cu$_2$) | 4.980  | $-0.1460$       | $(1.810, 1.0, 180^\circ)$          | 9.960  | $-0.025$        | $(1.810, 3.01, 180^\circ)$        |

Table 3 Crystallographic characteristics and parameters of magnetic couplings ($J_n$) calculated on the basis of structural data and respective distances between magnetic ions in pyrite $K_4Cu_4O_2(SO_4)_4Cu_0.5Cl_5$ (Data for ICSD no. 64684).
Table 3 (continued)

| Compound | Space group | Dimensionality | J \(_{\text{Cu1}}\) | J \(_{\text{Cu2}}\) | J \(_{\text{Fe–Cu1}}\) | J \(_{\text{Cu2–Fe}}\) |
|----------|-------------|----------------|----------------|----------------|----------------|----------------|
| K\(_4\)Cu\(_4\)O\(_2\)(SO\(_4\))\(_4\)Cl \(_{16}\) | I \(_a\) \(_4\) (N79): \(a = 13.60\ \text{Å}, b = 13.60\ \text{Å}, c = 4.98\ \text{Å}, \alpha = 90^\circ, \beta = 90^\circ, \gamma = 90^\circ\) | \(Z = 2\) | \(6.169\ \text{Å}\) | \(6.805\ \text{Å}\) | \(7.947\ \text{Å}\) | \(8.567\ \text{Å}\) |

Extra intrachain couplings (Table 2, Fig. 2d) at long distances \(J_{11}(J_{11}/J_1 = 0.21, d(\text{Cu1–Cu2}) = 5.664 \text{ Å})\) and \(J_{12}(J_{12}/J_1 = 0.22, d(\text{Cu1–Cu2}) = 5.791 \text{ Å})\) are also of the FM type, but they are almost fivefold weaker than the main ones along the tetrahedral edges. The FM couplings \(J_{1b}^\text{Cu1}\) \((J_{1b}^\text{Cu1}/J_1 = 0.23)\) and \(J_{1b}^\text{Cu2}\) \((J_{1b}^\text{Cu2}/J_1 = 0.28)\) between similar ions located at a distance of the \(b\) parameter of the unit cell are slightly stronger. Antiferromagnetic but very weak couplings \(J_{1c}^\text{Cu3}\) \((J_{1c}^\text{Cu3}/J_1 = 0.04, d(\text{Cu3–Cu3}) = 4.94 \text{ Å})\) and \(J_{1b}^\text{Fe}\) \(d(\text{Fe–Fe}) = 4.94 \text{ Å}\) exist between similar Cu3 and Fe atoms located through the \(b\) parameter. The AFM character of these couplings indicates to at least twofold increase of the \(b\) parameters of the magnetic unit cell, as compared to that in the crystal unit cell.

The weak AFM couplings \(J_{15}\) \((J_{15}/J_1 = 0.07, d(\text{Cu2–Cu2}) = 6.333 \text{ Å})\), \(J_{16}\) \((J_{16}/J_1 = 0.02, d(\text{Cu2–Cu3}) = 6.399 \text{ Å})\), \(J_{17}\) \((J_{17}/J_1 = 0.006, d(\text{Cu1–Cu1}) = 6.805 \text{ Å})\), \(J_{18}\) \((J_{18}/J_1 = 0.11, d(\text{Cu3–Cu3}) = 7.722 \text{ Å})\), and \(J_{19}\) \((d(\text{Fe–Cu1}) = 7.947 \text{ Å})\) (Table 2, Fig. 2d) exist between tetrahedral chains. According to the calculations, just one AFM interchain coupling \(J_{20}\) \((J_{20}/J_1 = 0.34, d(\text{Cu1–Cu2}) = 8.567 \text{ Å})\) is relatively strong. However, the strength of this coupling can be overestimated, since the decrease of coupling strengths accelerates along with the increase of distance.

To sum up, our calculations yielded a quasi-one-dimensional spin-tetrahedron system K\(_3\)Cu\(_3\)(Fe\(_{0.32}\)Al\(_{0.18}\))O\(_2\)(SO\(_4\))\(_4\), in which frustrated antiferromagnetic tetrahedra are linked through common edges into chains stretched along the \(b\) axis. All the couplings between nearest neighbors of copper and iron atoms inside the chain are themselves frustrated due to their location in tetrahedral vertices. Besides, extra competition of these AFM couplings with those between next-to-nearest neighbors Cu and Fe atoms in J\(_{11–J_{10–J_{6}}}, J_{12–J_{9–J_{5}}}, J_{13–J_{10–J_{1}}, J_{14–J_{7–J_{5}}, J_{14–J_{8–J_{6}}}}\) triangles exists inside the chain. Antiferromagnetic couplings between chains are very weak.

### 3.2 Piipite (Caratiite), K\(_4\)Cu\(_4\)O\(_2\)(SO\(_4\))\(_4\)MeCl

Piipite K\(_4\)Cu\(_4\)O\(_2\)(SO\(_4\))\(_4\)MeCl \((16)\) crystallizes in the noncentrosymmetric tetragonal \(I\) \(_4\) system. Just like in klyuchevskite, chains of edge-sharing oxo-centered OC\(_4\) tetrahedra serve as a base of the crystal structure of piipite (Fig. 3a). These chains are stretched in parallel to [001] and linked by SO\(_4^{2–}\) and K\(^{+}\) ions into a framework, whose channels contain Me and Cl\(^{−}\) ions. However, the nature of the Me atoms is not yet established completely. As was assumed in \((16), most probably, the position is half occupied by Cu\(^{2+}\), fully occupied by Na\(^{+}\), or occupied by a mixture of the two. Unlike klyuchevskite, in piipite, the chains of edge-sharing OC\(_4\) tetrahedra are polarized. The O1
The chain $[\text{Cu}_3\text{Fe}^{3+}\text{O}_2\text{(SO}_4)_4]^{3-}$ in the klyuchevskite $\text{K}_3\text{Cu}_3(\text{Fe}_{0.82}\text{Al}_{0.18})\text{O}_2\text{(SO}_4)_4$ along the $b$ axis. The sublattice of magnetic ions Cu$^{2+}$ and Fe$^{3+}$ and the coupling $J_n$ in klyuchevskite. 

The chain of edge-sharing (Cu$_3$Fe) tetrahedra. 

The corrugated chain of copper triangles alternately linked through the side and vertex in case of Fe$^{3+}$ ion substitution by nonmagnetic ions. 

Intrachain and interchain $J_n$ couplings. In this and other figures, the thickness of lines shows the strength of $J_n$ coupling. AFM and FM couplings are indicated by solid and dashed lines, respectively. The possible FM $\rightarrow$ AFM transitions are shown by the stroke in dashed lines.

According to our calculations, the AFM nearest neighbor $J_1$ ($J_1 = -0.0719 \text{ Å}^{-1}$, $d$(Cu1–Cu1) = 2.936 Å) and $J_2$ ($J_2/J_1 = 0.96$, $d$(Cu1–Cu1) = 3.242 Å) couplings of Cu$_4$ tetrahedra linked through common edges into chains parallel to the $c$ axis are the dominating ones (Table 3, Fig. 3b). The contribution to AFM components of these couplings emerges under the effect of oxygen ions (O1) centering the chains of Cu$_4$ tetrahedra.

The possible FM $\rightarrow$ AFM transitions are shown by the stroke in dashed lines.

Polarization along the $c$ axis of the chain of edge-sharing OCu$_4$ tetrahedra in piipite $\text{K}_4\text{Cu}_4\text{O}_2\text{(SO}_4)_4\text{MeCl}$ a. The sublattice of magnetic ions Cu$^{2+}$ formed from chains of edge-sharing (Cu$_4$) tetrahedra and the coupling $J_n$ in piipite b. The interchain $J_n$ couplings in case of occupancy of Me positions by magnetic Cu$^{2+}$ ions (projection of the structure parallel to [001]) c.
above tetrahedra. Just like $J_1$ couplings, the next-to-nearest neighbor $J_3$ and $J_4$ intrachain couplings are also antiferromagnetic, but three- and sixfold weaker, respectively. All these couplings compete to each other, while tetrahedral chains in piipite are frustrated.

Just one coupling $J_c (J_c/J_1 = -0.06, d(Cu1–Cu1) = 4.980 \text{ Å})$ between copper ions in the chain located across the $c$ parameter is very weak and ferromagnetic, but it also competes with the weak AFM $J_c (J_c/J_1 = 0.07)$ coupling that is the next along the $c$ parameter. Chains are located at large distances from each other. The nearest between chains $J5 (J5/J1 = -0.015, d(Cu1–Cu1) = 7.240 \text{ Å})$ coupling is very weak antiferromagnetic. The subsequent couplings at distances within 9 Å are weak ferromagnetic.

If one assumes that the Me position ($x = 0, y = 0, z = 0.448$) is at least half occupied by the magnetic Cu(2)(2)$^{2+}$ ion, then strong AFM $J7 (J7/J1 = 0.86, d(Cu1–Cu1) = 6.169 \text{ Å})$ and weaker AFM $J9 (J9/J1 = 0.15, d(Cu1–Cu1) = 6.238 \text{ Å})$ and FM $J8 (J8/J1 = -0.10, d(Cu1–Cu1) = 6.028 \text{ Å})$ couplings will emerge between frustrated tetrahedral chains and Cu2 ions.

If the Me position was fully occupied with magnetic Cu2$^{2+}$ ions, then the piipite structure would consist of two types of chains stretched along the $c$ axis: linear chains – Cu2–Cu2– of strong AFM $J_c(Cu2)$ couplings formed due to intermediate Cl$^-$ ions and frustrated chains of AFM Cu14 tetrahedra (Table 3, Fig. 3c). These chains are linked to each other through strong AFM $J7$ couplings.

However, coordination in the form of a virtually regular octahedron is not characteristic of the Cu2$^{2+}$ ion. It is more similar to the coordination of the nonmagnetic Cu1$^{1+}$ ion, if one considers two collinear axial Cu–Cl bonds (2.49 Å) as shortened ones for large chloride ions and, in addition, four elongated Cu–O5 bonds (2.50 Å) with small oxygen ions in the octahedron equatorial plane.

To sum up, the results of calculations of characteristics of magnetic couplings by the crystal chemistry method and the analysis of their competition in the structures of noncentrosymmetric minerals klyuchevskite ($K_3Cu_3(Fe_{0.82}Al_{0.18})O_2(SO_4)_4$) and piipite ($K_4Cu_4O_2(SO_4)_4Cu_0.5Cl$) assume that their magnetic structures comprise quasi-one-dimensional systems. The magnetic structures of these minerals are formed by dominating in strength antiferromagnetic chains of edge-sharing tetrahedra. All the couplings in chains are frustrated. Antiferromagnetic and ferromagnetic couplings between chains are very weak.

Besides, in piipite, the strong frustration of magnetic interactions (the absence of magnetic ordering) is combined with the presence of electric polarization in tetrahedral chains. The O1 ions centering Cu4 tetrahedra are shifted from the tetrahedron center along the 001 direction (Fig. 3a). This polarization can be also considered as the shift along the 00-1 direction of the chain of tetrahedra of Cu2$^{2+}$ cations relative to O2$^-$ anions centering these tetrahedra. Our calculations demonstrate that the shift of the O1 ion to the tetrahedron center (at preservation of acceptable Cu–O bond lengths) will yield substantial changes in neither strength nor character of magnetic couplings, since the position occupied by the O1 ion is not a critical one.

### 3.3 Uniqueness of Tetrahedral Spin Chains in Klyuchevskite and Piipite

Magnetism of tetrahedral spin chains is of great interest for theoretical and experimental studies. In the literature, zigzag-like chains of corner-sharing tetrahedra [2–6] (Fig. 4a), the tetrahedral-cluster spin chain [48–50] (Fig. 4b), and the chain of edge-sharing tetrahedra [51, 52] (Fig. 4c) are considered as quasi-one-dimensional frustrated spin-tetrahedral systems.

Among these three tetrahedral quasi-one-dimensional spin systems, the only widely spread one contains corner-sharing tetrahedral chains, for instance in Cu3Mo2O9 [53, 54] and in pyrochlore lattices [30]. We did not manage to find in the literature any data on experimental studies of magnetic compounds, in which spin tetrahedra would be linked into chains via edges.

Instead of the tetrahedral-cluster spin chain and the spin chain of edge-sharing tetrahedra, the system Cu2Te2O5X2 with $X = \text{Cl, Br}$ has been examined in the literature [36, 37, 56, 57]. It contains tetrahedral clusters of copper ions (Cu4), which are not edge-sharing, but align to tubes or chains. Strong inter-tetrahedral couplings are present in

![Graphical representation](Image)

**Fig. 4** Schematic representation of quasi-one-dimensional frustrated spin-tetrahedral systems a Zigzag-like chains of corner-sharing tetrahedra. b Tetrahedral-cluster spin chain. c Chain of edge-sharing tetrahedra. d Chains in Cu2Te2O5X2
such chains. However, in spite of numerous theoretical and experimental studies, the accurate dimensionality of the Cu$_2$Te$_2$O$_5$X$_2$ system is not clear. There exists the opinion that this system is three-dimensional rather than quasi-one-dimensional, since interchain interactions in it are rather strong [7, 37, 56, 57]. Different models of the magnetic state of this system were examined in theoretical terms. The authors of Refs. [49–51] investigated frustration in the tetrahedral-cluster spin chain and the chain of edge-sharing tetrahedra within the frames of the model of two-leg spin ladders. Kotov et al. [58, 59] demonstrated the role of antisymmetric Dzyaloshinsky–Moriya (DM) [60, 61] spin–spin interactions in inducing weak antiferromagnetism in Cu$_2$Te$_2$O$_5$Br$_2$.

We found frustrated AFM spin chains of edge-sharing tetrahedra (Fig. 4b) in two minerals: klyuchevskite and piipite. The uniqueness of these minerals consist not only in the very presence of such spin-tetrahedral chains in them but also in the fact that the AFM character and frustration of exchange interactions in these chains are caused by oxygen ions centering copper tetrahedra (OCu$_4$). Since the shift of these oxygen ions is limited by small sizes of Cu$_4$ tetrahedra, reorientation of magnetic moments (AFM→FM) along the tetrahedral edges and, therefore, the frustration suppression due to changes in the character of exchange interactions in the chain will be impossible.

4 Conclusions

As was demonstrated by the calculations of the sign and strength of magnetic interactions based on the structural data, noncentrosymmetric minerals klyuchevskite (K$_2$Cu$_3$(Fe$_{0.82}$Al$_{0.18}$)O$_2$(SO$_4$)$_4$) and piipite (K$_4$Cu$_4$O$_2$(SO$_4$)$_4$MeCl) were frustrated quasi-one-dimensional spin = 1/2 tetrahedral systems containing AFM spin chains of edge-sharing Cu$_4$ tetrahedra. The magnetic system of such compounds is disordered because of frustration of strong exchange interactions in tetrahedra, in which antiparallel orientation of all the nearest neighbors is impossible due to geometric reasons. At the same time, in the crystal structure of piipite, one detects the existence of electric ordering (polarization) of chains of OCu$_4$ tetrahedra, since the oxygen O1 ions that center them are shifted from the tetrahedral centers along the 001 direction.

In conclusion, one should mention some problems inherent to determination of the crystal structure of these minerals, but they cannot be solved by crystal chemistry methods. Although the existence of frustration of magnetic interactions in these minerals is caused by their crystal structures and raises no doubts, it is still unclear whether their magnetic systems will remain completely disordered until the temperature absolute zero (will become the quantum spin liquid). In view of this, it appears of interest to reveal the possibility of having an essential role in magnetic ordering for very weak long-range AFM interactions linking base elements of the magnetic structure (frustrated tetrahedral chains with strong AFM interactions). Another problem consists in the possibility of the emergence of the spatially modulated spin structure in these minerals as a result of activation of forces of the relativistic nature (of Dzyaloshinsky–Moriya) [60, 61]. The crystal structures of klyuchevskite and piipite are favorable for this, since their space groups (I2 and I4, respectively) do not contain the inversion center, symmetry planes, and rotoinversion axes.

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