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# A novel germanate, $\text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13}$ , with a four tetrahedra oligomer

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## Abstract

The structure of  $\text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13}$ , previously thought to be  $\text{CuFeGe}_2\text{O}_6$ , has been determined from single-crystal X-ray diffraction data to be monoclinic,  $P2_1/m$ ,  $a = 12.1050(6)$ ,  $b = 8.5073(4)$ ,  $c = 4.8736(2)$  Å,  $\beta = 96.145(1)^\circ$ ,  $Z = 2$ , with  $R1 = 0.0231$  and  $wR2 = 0.0605$ . The unique structure has an oligomer of four germanate tetrahedra, cross-linked laterally by square-planar copper ions, joined end-to-end by a zigzag chain of edge-sharing iron oxide octahedra. Running along the  $a$ -direction the metal oxide chain consists of alternating Cu–Cu and Fe–Fe dimers. A hypothetical series of homologous structures ( $\text{Cu}_{n-2}\text{Fe}_2\text{Ge}_n\text{O}_{3n+1}$  with  $n = 3, 4, \dots, \infty$ ) with different length germanate oligomers is proposed, where as  $n$  increases, the infinite chain of the  $\text{CuGeO}_3$  is approached. In this context,  $\text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13}$  is viewed as being built from blocks of  $\text{CuGeO}_3$  and the Fe oxide chains. This material has significance to the study of low-dimensional mixed-spin systems.

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**Keywords:** Germanate;  $\text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13}$ ; Crystal structure; Mixed-spin system;  $\text{CuGeO}_3$ ; Low-dimensional magnet

## 1. Introduction

Quantum spin systems have been studied extensively in condensed matter physics, which has resulted in a good understanding of simple model systems. One of the new challenges in this area is greater complexity, such as that offered by mixed-spin systems. The mixed spins chain with period 4, such that the spins are arrayed as  $s_a - s_a - s_b - s_b$  in the unit cell, has been a focus of theoretical interest [1–4] and rich phase diagrams of the ground states have been presented. A model material of this system; however, has not been reported.

Many low-dimensional spin materials are reported in germanates, where a tetrahedral germanate chain separates the transition metal spin chain, such as the spin Peierls materials  $\text{CuGeO}_3$  [5,6]. Therefore, a trial germanate which contains two different 3d transition metals would seem to be a good strategy to discover a mixed-spins chain material.

Previously,  $\text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13}$  was thought to be  $\text{CuFeGe}_2\text{O}_6$ , but the crystal structure had not been deter-

mined. It is the only known ternary phase in the  $\text{CuO-GeO}_2-(1/2)\text{Fe}_2\text{O}_3$  system. Here we report the crystal structure, describe its relationship to  $\text{CuGeO}_3$ , and discuss its possibility as a low-dimensional mixed-spin system.

## 2. Experimental

A rod-shaped polycrystalline sample of the title compound was synthesized by solid state reaction methods. The mixture of starting materials,  $\text{CuO}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{GeO}_2$ , was heated at  $1000^\circ\text{C}$  in air for 50 h. This compound melts congruently and a large single crystal was easily grown from the polycrystalline starting material by the floating zone method using an infrared image furnace. The size of the crystal grown was about 3 mm in diameter by 3 cm in length. A small slice of one end of the boule was cut off, and broken to obtain a small crystal suitable for X-ray diffraction measurements. The cleavage fragment selected exhibited uniform optical properties and is pleochroic, green to darker green. The one good cleavage plane was later

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determined to be  $\{110\}$ . Single-crystal X-ray diffraction data were collected at room temperature using a Bruker AXS SMART 1000 diffractometer equipped with a CCD area detector and a graphite monochromatized Mo source ( $K\alpha$ , 0.71073 Å). The crystal-to-detector distance was 5 cm. More than a hemisphere of data were collected over the angular range  $3^\circ \leq 2\theta \leq 56.7^\circ$ . Frame widths of  $0.2^\circ$  were used for the data collection, counting 20 s per frame. The three dimensional data were integrated and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. Unit cell dimensions were refined on the basis of 4678 reflections by least-squares methods. An empirical absorption correction was made using SADABS [7]. Systematic absences were consistent with the space group  $P2_1/m$ . A total of 5151 reflections was collected, and merging of equivalent reflections gave 1283 unique reflections ( $R_{\text{int}} = 3.3\%$ ), with 1233 classed as observed ( $|F_o| \geq 4\sigma_F$ ). The structure was solved by direct methods using SIR97 [8]. Crystal structure refinement was made using SHELX [9] packaged in the WinGX suite [10]. Data collection parameters and refinement results are given in Table 1. Scattering factors for neutral atoms, together with anomalous dispersion corrections, were taken from *International Tables for Crystallography* [11]. Refinement with anisotropic atomic displacement parameters was made, but

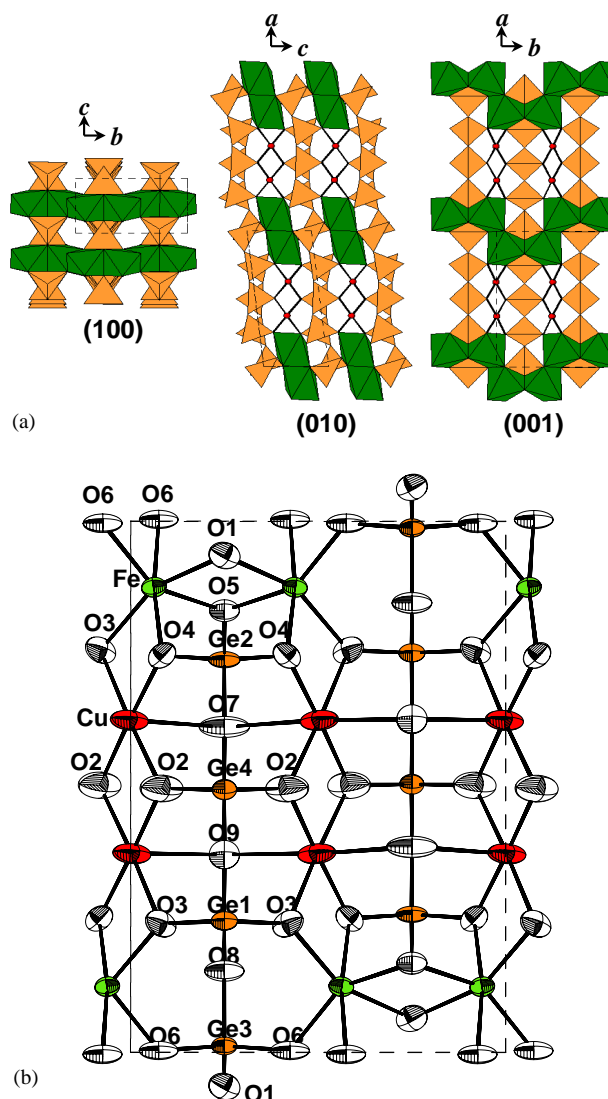


Fig. 1. (a) Crystal structure projections of  $\text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13}$ , with the iron oxide octahedra darkly shaded and the germanate tetrahedra lightly shaded. The square-planar Cu oxide units are shown as ball-and-stick. The unit cell is outlined by a dashed box for each projection. (b) Probability (99%) density ellipsoids showing the root-mean-square displacements of the atoms in a (001) projection of the unit cell outlined by the dashed line.

Table 1  
Data collection parameters and refinement results for  $\text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13}$

$a$ (Å)	12.1050(6)
$b$ (Å)	8.5073(4)
$c$ (Å)	4.8736(2)
$\beta$ (deg)	96.145(1)
$V$ (Å <sup>3</sup> )	499.00(4)
Space group	$P2_1/m$
$Z$	2
Formula	$\text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13}$
Formula weight (g)	737.14
Crystal dimensions (mm)	$0.10 \times 0.10 \times 0.02$
$\mu$ (mm <sup>-1</sup> )	18.95
Color	green
Cleavage	$\{110\}$ good
Density calc. (g/cm <sup>3</sup> )	4.906
$F(000)$	684
Number of variables	110
Extinction coefficient	0.062(1)
Measured reflections	5151
Unique reflections	1283
Unique reflections $I > 4\sigma_F$	1233
Goof = $S$	1.14
$R_{\text{int}}$	0.033
$R1_{\text{obs}}$	0.0231
wR2	0.0605
Weight	$1/[\sigma^2(F_o^2) + (0.0357P)^2 + 0.1616P]$
	$P = (F_o^2 + 2F_c^2)/3$
Max., min., $\Delta\rho$ e Å <sup>-3</sup>	-1.22, 1.23

only the refinement with equivalent isotropic displacement parameters is reported. Polyhedral drawings projected on the principal planes are displayed in Fig. 1a and the probability ellipsoids for the root-mean-square atomic displacements are shown in Fig. 1b along with the atomic numbering scheme. The atomic positions and isotropic displacement parameters are given in Table 2 and selected bond lengths and angles particularly relevant to the mixed-spin system geometry are given in Table 3. The anisotropic displacement parameters are archived with the crystallographic information file.

Table 2  
Atomic positional and displacement parameters for  $\text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13}$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> (nm <sup>2</sup> )	Symmetry
Cu	0.62557(2)	0.49662(3)	0.54329(6)	1.00(1)	1
Fe	0.87587(2)	0.56133(4)	0.54825(6)	0.49(1)	1
Ge1	0.73996(3)	3/4	0.99333(7)	0.48(1)	<i>m</i>
Ge2	0.50508(3)	1/4	0.09433(8)	0.60(1)	<i>m</i>
Ge3	0.75264(3)	1/4	0.16240(8)	0.49(1)	<i>m</i>
Ge4	0.98773(3)	1/4	0.89357(7)	0.45(1)	<i>m</i>
O1	0.7477(1)	0.5840(2)	0.7848(4)	0.79(4)	1
O2	0.4969(1)	0.5828(3)	0.7025(4)	1.43(4)	1
O3	0.7578(1)	0.4201(2)	0.3655(4)	0.82(4)	1
O4	0.9963(1)	0.4253(2)	0.7081(4)	0.71(4)	1
O5	0.8315(1)	3/4	0.2951(5)	0.66(5)	<i>m</i>
O6	0.3869(1)	1/4	0.8547(5)	0.83(5)	<i>m</i>
O7	0.8465(2)	1/4	0.9275(6)	1.37(6)	<i>m</i>
O8	0.6274(1)	1/4	0.9338(5)	0.90(6)	<i>m</i>
O9	0.0642(2)	1/4	0.2198(5)	0.75(5)	<i>m</i>

$P2_1/m$ ,  $a = 12.1050(6)$ ,  $b = 8.5073(4)$ ,  $c = 4.8736(2)$  Å,  $\beta = 96.145(1)^\circ$ ,  $V = 499.00(4)$  Å<sup>3</sup>.

Table 3  
Selected interatomic distances (Å) and bond angles (deg) for  $\text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13}$

Ge1–O1	1.748(1) × 2	Cu–O1–Fe	101.39(8) ( <i>~a</i> direction)
Ge1–O5	1.745(2)	Cu–O2–Cu × 2	102.38(9) ( <i>~a</i> direction)
Ge1–O6	1.776(2)	Cu–O3–Fe	100.23(8) ( <i>~a</i> direction)
Mean	1.754	Fe–O4–Fe	107.29(8) ( <i>b</i> direction)
Ge2–O2	1.735(2) × 2	Fe–O5–Fe × 2	102.3(1) ( <i>~a</i> direction)
Ge2–O6	1.747(2)	Fe–O9–Fe	103.0(1) ( <i>b</i> direction)
Ge2–O8	1.748(2)	Cu...Cu	3.0247(3) ( <i>a</i> direction)
Mean	1.741	Fe...Cu	3.0770(3) ( <i>~a</i> direction)
Ge3–O3	1.750(1) × 2	Fe...Fe	3.2625(4) ( <i>~a</i> direction)
Ge3–O7	1.697(3)		3.2101(6) ( <i>b</i> direction)
Ge3–O8	1.782(2)		
Mean	1.744		
Ge4–O4	1.753(1) × 2		
Ge4–O7	1.735(2)		
Ge4–O9	1.751(2)		
Mean	1.748		
Fe–O1	2.038(1)		
Fe–O3	2.001(1)		
Fe–O4	1.956(1)		
Fe–O4	2.092(1)		
Fe–O5	2.060(1)		
Fe–O9	2.050(1)		
Mean	2.032		
Cu–O1	1.937(1)		
Cu–O2	1.926(1)		
Cu–O2	1.955(1)		
Cu–O3	2.008(1)		
Cu–O6	2.892(1)		
Cu–O8	2.831(1)		
Mean	1.964 (CN 4)		
Mean	2.258 (CN 4+2)		

### 3. Results

Based on the chemical formula,  $\text{CuFeGe}_2\text{O}_6$ , and lattice parameters ( $a = 12.08$ ,  $b = 8.502$ ,  $c = 4.878$  Å,  $\beta = 96.25^\circ$ ) given on the PDF card 38-1177 by M. Behruzzi and Th. Hahn, it was thought that the crystal structure might be a distorted pyroxene; however, this is not the case. The correct structural formula is  $\text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13}$ . The structure is unique in having an oligomer of four germanate tetrahedra, cross-linked laterally by square-planar copper ions, joined end-to-end by a zigzag chain of edge-sharing iron oxide octahedra. The square-planar coordination geometry of Cu has four bond lengths between 1.926(1) and 2.008(1) Å; the next-nearest oxygen atoms at 2.831(1) and 2.892(1) Å complete a (4+2) coordination due to a large Jahn–Teller distortion. The transition metal oxide polyhedra form edge-sharing chains. Running along the *a*-direction the metal oxide chain consists of alternating Cu–Cu and Fe–Fe dimers. The chains are linked along the *b*-direction by a zigzag Fe oxide chain. All of the anions belong to the germanate tetrahedra,  $[\text{Ge}_4\text{O}_{13}]^{10-}$ , making the tetrahedral sharing coefficient according to Zoltai [12] equal to 1.375. The bond valence sums to all of the oxygen atoms are perfectly satisfied only if the valence of the Cu and Fe are +2 and +3, respectively. The ternary phase diagram,  $\text{CuO–GeO}_2\text{–}(1/2)\text{Fe}_2\text{O}_3$ , appropriately contoured with different values of Zoltai's tetrahedral sharing coefficient [13] (Fig. 2), shows the compositional range of a hypothetical series

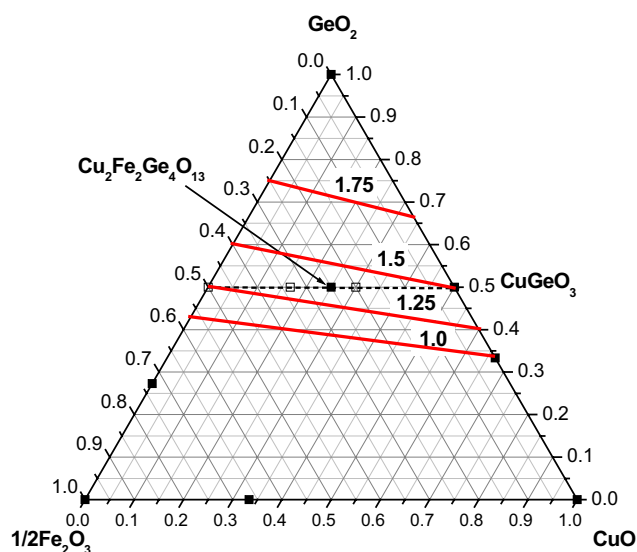


Fig. 2. The ternary phase diagram,  $\text{CuO–GeO}_2\text{–}(1/2)\text{Fe}_2\text{O}_3$ , in molar quantities. The bold lines are contours for different values of Zoltai's tetrahedral sharing coefficient [12,13] and are so labeled. Hypothetical (open symbols) and observed (solid symbols) compounds of the hypothetical homologous structural series  $(\text{Cu}_{n-2}\text{Fe}_2\text{Ge}_n\text{O}_{3n+1})$  with  $n = 2, 3, 4, \dots, \infty$  plot along the dashed line between hypothetical  $\text{Fe}_2\text{Ge}_2\text{O}_7$  and the well-known  $\text{CuGeO}_3$ .

of homologous structures ( $\text{Cu}_{n-2}\text{Fe}_2\text{Ge}_n\text{O}_{3n+1}$  with  $n = 3, 4, \dots, \infty$ ) with different length germanate oligomers. As the oligomer length,  $n$ , increases, the infinite chain of the  $\text{CuGeO}_3$  is approached. The hypothetical structures of  $n = 3, 5, 6, \dots$  are crystal chemically reasonable in terms of Pauling's electrostatic neutrality principle; however, their realization might only be possible in engineered thin film superlattices. The  $n = 2$  member, containing no copper, is problematic because it would require the condensation of the iron oxide octahedral chains into a trioctahedral (gibbsite-type) sheet, which would result in some of the oxygen atoms being underbonded. The symmetry of the  $n = 3$  phase is expected to also be monoclinic with a slightly larger  $\beta$  angle than for the  $n = 4$  phase. For the  $n = 5$  and higher phases the  $\beta$  angle is expected to gradually change towards  $90^\circ$ . The  $d(100)$ -spacings of the hypothetical phases will be commensurate with the reduction or increase of multiples of the  $\text{CuGeO}_3$  layer module thickness (Fig. 3); 2.9349(4) Å in  $\text{CuGeO}_3$  [14] compared to 3.0088 Å for the same layer module in  $\text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13}$ . Indeed the  $b$  and  $c$  lattice parameters, 8.5073(4) and 4.8736(2) Å, of  $\text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13}$  are only slightly expanded as compared to their corresponding  $c$  and  $b$  lattice parameters, 8.449(2) and 4.786(1) Å, of  $\text{CuGeO}_3$  [14]. The Jahn–Teller coordination geometry of the Cu in  $\text{CuGeO}_3$  (1.934 and 2.746 Å) is also slightly less distorted than in  $\text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13}$  (Table 3). Preliminary attempts to synthesize the  $n = 3$  and 5 members by solid-state methods were not successful.

The oligomeric germanate anion in this structure is unusual and hitherto has rarely been observed in either germanates or silicates. Stabilization of the germanate oligomers seems to be achieved by the size and charge match of the edge-sharing, (4+2)-coordinated copper oxide groups which join them together, as in  $\text{CuGeO}_3$ . The mineral kinoite,  $\text{Ca}_2\text{Cu}_2\text{Si}_3\text{O}_{10}(\text{H}_2\text{O})$  [15], has a triple-tetrahedra silicate oligomer in which a square-pyramidal, edge-sharing, copper oxide chain is present,

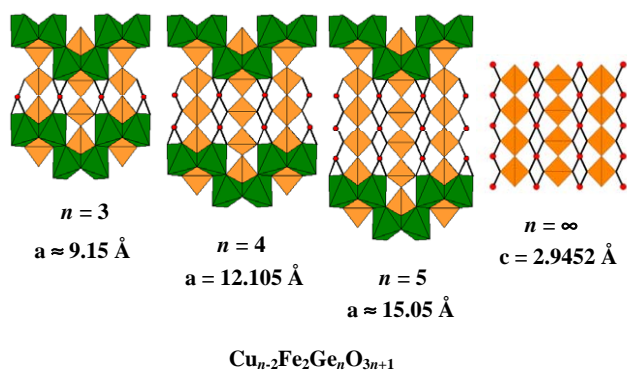


Fig. 3. (001) Crystal structure projections of the proposed homologous series  $\text{Cu}_{n-2}\text{Fe}_2\text{Ge}_n\text{O}_{3n+1}$  for  $n = 3, 4, 5$ , and  $\infty$ . Coordinates for  $\text{CuGeO}_3$  ( $n = \infty$ ) were taken from Braden et al. [14].

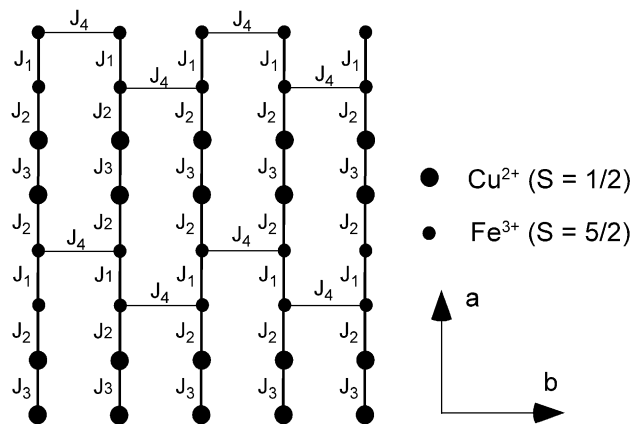


Fig. 4. Topology of the possible spin structure of  $\text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13}$  built from the  $\text{Fe}^{3+}$  ( $S = 5/2$ ) and  $\text{Cu}^{2+}$  ( $S = 1/2$ ) projected on (001).

but the structure is topologically quite different from that of  $\text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13}$  and would not be a member of the proposed homologous series. A four-tetrahedra oligomer is found in the crystal structure of the silicate  $\text{Nd}_2\text{Ba}_2\text{Si}_4\text{O}_{13}$  [16] as well as several other phosphates, vanadates, and chromates.

From the point of view of quantum spin systems, spin  $S = 1/2$  is localized at the  $\text{Cu}^{2+}$  ( $3d^9$ ) ion and spin  $S = 5/2$  is localized at the  $\text{Fe}^{3+}$  ( $3d^5$ ) ion. Through anion superexchange, interaction exists between the magnetic ions in general. A mixed-spins chain with period 4, such that the spins are arrayed as  $S = 1/2, S = 1/2, S = 5/2, S = 5/2$ , extends in the  $a$ -direction and a zigzag  $S = 5/2$  is along the  $b$ -direction, which together form a two-dimensional spin plane (Fig. 4). Four different spin interactions ( $J_1, J_2, J_3$ , and  $J_4$ ) are expected. The spin plane is separated by oligomers of four germanate tetrahedra,  $[\text{Ge}_4\text{O}_{13}]^{10-}$ , and therefore, this compound is a model material for a low-dimensional mixed-spin system.

Success in the synthesis of  $\text{Cu}_{n-2}\text{Fe}_2\text{Ge}_n\text{O}_{3n+1}$  ( $n \geq 5$ ) will give us model materials for the study of finite chain effects in the spin-Peierls system. There are many studies of impurity effects in doped spin-Peierls materials, e.g.,  $\text{Cu}_{1-x}\text{Zn}_x\text{GeO}_3$  [17],  $\text{CuGe}_{1-x}\text{Si}_x\text{O}_3$  [18],  $\text{Cu}_{1-x}\text{Mg}_x\text{GeO}_3$  [19,20]. In these cases, impurities are distributed randomly and therefore both randomness and finite chain effects have to be considered. In contrast, for  $\text{Cu}_{n-2}\text{Fe}_2\text{Ge}_n\text{O}_{3n+1}$  ( $n \geq 5$ ) it will be possible to study the finite chain effect systematically.

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