

Disorder of the Water Molecules and Sulfate Anion in the Crystal Structure of Fe-substituted Synthetic Chalcantite Crystals ($\text{Cu}_{1-x}\text{Fe}_x$) $\text{SO}_4 \cdot 5\text{H}_2\text{O}$ ($x = 0.1$ and 0.20)

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The crystal structures of two chalcantites, $(\text{Cu}_{0.90}\text{Fe}_{0.10})\text{SO}_4 \cdot 5\text{H}_2\text{O}$ (I) and $(\text{Cu}_{0.80}\text{Fe}_{0.20})\text{SO}_4 \cdot 5\text{H}_2\text{O}$ (II), were determined by single-crystal X-ray diffraction at room temperature. The crystallographic data are (I), triclinic $P\bar{1}$, $Z = 2$, $a = 5.9642(3)$, $b = 6.1186(3)$, $c = 10.7128(5)\text{Å}$, $\alpha = 77.340(4)$, $\beta = 82.384(4)$, $\gamma = 72.633(4)^\circ$, $V = 363.13(3)\text{Å}^3$, $R = 0.036$; (II), triclinic $P\bar{1}$, $Z = 2$, $a = 5.9611(6)$, $b = 6.1270(6)$, $c = 10.7101(9)\text{Å}$, $\alpha = 77.200(8)$, $\beta = 82.314(8)$, $\gamma = 72.484(9)^\circ$, $V = 362.82(6)\text{Å}^3$, $R = 0.0701$. Both of the crystal structures are isostructural with chalcantite, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and composed of the square-planar $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ ion at the M1 site and the $[(\text{Cu,Fe})(\text{H}_2\text{O})_4]^{2+}$ ion at the M2 site, and the SO_4 tetrahedra which acts as a μ_2 -bridge between these sites and one water molecule crystallization. However, unlike chalcantite, in both crystals aqua ligands at the M2 site are disordered over two positions, and in the second crystal the O atoms of sulfate group are disordered over two positions. The O atoms of the disordered aqua ligands surrounding the Cu2 atom are with occupation factors $0.42(4)/0.58(4)$ and $0.47(2)/0.53(2)$ for structure (I), and, $0.50(7)/0.50(7)$ and $0.7(1)/0.3(1)$ for structure (II).

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The isomorphism and isodimorphism of the d metal sulfates are of particular importance for the crystal chemistry of minerals, materials science, solid solutions physics and processing of the ores. The thermodynamic theory of solid-solution aqueous-solution interactions and available the effects of ionic substitutions on the thermodynamic properties of binary sulfate solid solutions were discussed before in detail.¹ Chalcantite is paramagnetic compound, and doping another paramagnetic atom, Fe^{2+} , to it allow to modify its magnetic susceptibility.² Crystals of chalcantite have an optical band pass with a transmission band of $0.280 - 0.570$ nm with a maximal transmission of 75%; they can be successfully used as an optical bandpass in higher resolution spectral devices.³ Some Fe-containing chalcantite crystals were studied by the single crystal X-ray diffraction method and the distribution of the Cu and Fe atoms over the crystallographic sites are determined by using of the results of analytical chemistry or according to the degree of the distortion of the coordination polyhedrons around sites.^{4,5} Site occupations of the Cu and Fe atoms are not possible because of the similar scattering-factors of these elements. To except the problems of non-distinguishability of Cu and Fe during an X-ray diffraction study, we have synthesized the solid solutions of chalcantite with a priori known chemical compositions, $(\text{Cu}_{0.90}\text{Fe}_{0.10})\text{SO}_4 \cdot 5\text{H}_2\text{O}$ (I) and $(\text{Cu}_{0.80}\text{Fe}_{0.20})\text{SO}_4 \cdot 5\text{H}_2\text{O}$ (II), and have studied (Fig. 1). The influence of substituting Cu for Fe ion on the structural disorders of the subunits in the crystal of chalcantite was not performed. For this reason, this work is aimed at an X-ray diffraction study of the crystal structure of these compounds.

Single crystals of (I) and (II) were synthesized by stirring 0.01 M sulfuric acid solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in molar of ratios of 9:1 and 8:2 at a temperature of $\sim 45^\circ\text{C}$, respectively. The X-ray diffraction data were collected on a Xcalibur, Ruby diffractometer using graphite-monochromated $\text{Cu-K}\alpha$ radiation. Crystal and experimental data details are given in the Table 1.

The values of the $|E^2 - 1|$ statistical parameters show that both crystals are centrosymmetric, and because its crystal structures were solved in the space group $P\bar{1}$ and refined by a full-matrix least-squares method.⁶ The hydrogen atoms were found from difference maps, though not refined. Disorder manifests itself as a splitting of the O atoms sites and trigonal planar configuration of the O atoms of aqua ligands. The perceptible residual electron density remain around the M2 site on the distance 0.52Å .

Both crystal structures are composed of the square-planar $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ located at the M1(0,0,0) site and $[(\text{Cu,Fe})(\text{H}_2\text{O})_4]^{2+}$ at the M2(0,1/2,-1/2) site. The SO_4 tetrahedra acts as a μ_2 -bridging ligand between these cations, which lead to a chain structure (Figs. 2 and 3). The water of crystallization takes place in the hydrogen bonds. Selected Cu-O bond lengths are presented in Table 2.

Refinements of the crystal structures (I) and (II) showed that the M1 site is occupied fully by the Cu, and the M2 site is shared by Cu and Fe with relatively site occupations of 0.80 and 0.20 for (I) and 0.60 and 0.40 for (II), respectively. The M1O_6 and M2O_6 octahedrons are distorted because the Cu^{2+} ion in the electronic configuration d^9 exhibits the Jahn-Teller effect. In the both structures, as well as in the crystal structure of chalcantite, the apical M1-O_{ap} bonds are shorter than the apical M2-O_{ap}

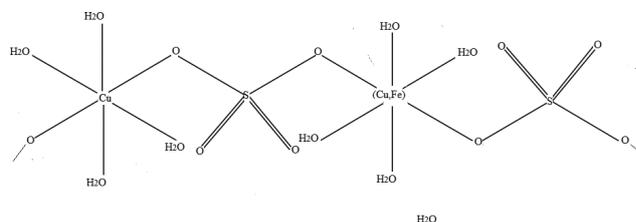


Fig. 1 Fragment of polymer chains in the title compounds.

Table 1 Crystal and experimental data

Chemical formula	(Cu _{0.90} Fe _{0.10})SO ₄ ·5H ₂ O	(Cu _{0.80} Fe _{0.20})SO ₄ ·5H ₂ O
Mr	248.91	248.14
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$
Temperature/K	293	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.9642(3), 6.1186(3), 10.7128(5)	5.9611(6), 6.1270(6), 10.7101(9)
α , β , γ (°)	77.370(4), 82.384(4), 72.633(4)	77.200(8), 82.314(8), 72.484(9)
<i>V</i> (Å ³)	363.13(3)	362.82(6)
<i>Z</i>	2	2
<i>D_s</i> /g cm ⁻³	2.276	2.271
Radiation:	Cu <i>K</i> α	Cu <i>K</i> α
μ (Cu <i>K</i> α)/mm ⁻¹	8.50	9.75
<i>F</i> (0 0 0)	407	253
Crystal size/mm	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.2
Data collection		
Diffractometer	Xcalibur, Ruby	Xcalibur, Ruby
Absorption correction	Multi-scan	Multi-scan
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	4823, 1493, 1481	2487, 1466, 1466
<i>R</i> _{int}	0.032	0.030
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.629	0.629
<i>E</i> ² - 1	0.894	0.903
<i>R</i> [<i>F</i> ₂ > 2 σ (<i>F</i> ₂)], <i>wR</i> (<i>F</i> ₂), <i>S</i>	0.036, 0.094, 0.76	0.0701, 0.1933, 1.08
No. of reflections	1493	1466
No. of parameters	144	167
No. of restraints	25	36
H-atom treatment	H-atom parameters are refined	H-atom parameters are refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ ⁻³)	0.72, -0.81	3.59, -3.02
Program system	SHELXL ⁶	SHELXL ⁶
CCDC deposition numbers	2076876	2076791

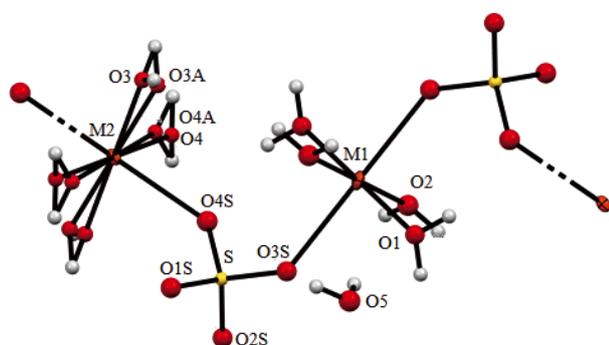


Fig. 2 Fragment of the polymer chain in the crystal structure I. Symbols of atoms are shown only for the asymmetric unit.

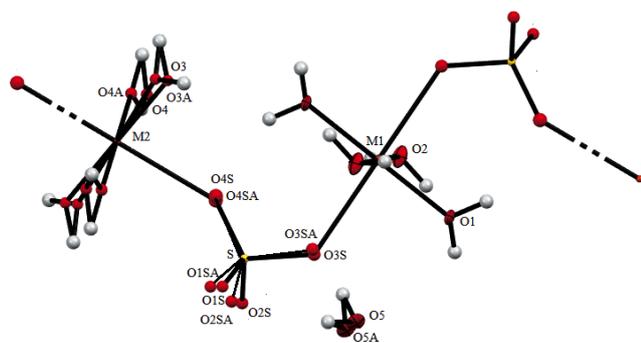


Fig. 3 Fragment of the polymer chain in the crystal structure II. The symbols of atoms and disordering of the sulfate group are shown only for the asymmetric unit.

Table 2 Selected bond distances (Å) in the structures I and II

Bond	I	II
M1-O1	1.973(2)	1.970(4)
M1-O2	1.965(2)	1.971(4)
M1-O3s	2.377(2)	2.346(9)
M1-O3sA	—	2.347(9)
M2-O3	1.959(2)	1.970(10)
M2-O3A	1.968(2)	1.968(8)
M2-O4	1.955(2)	1.969(12)
M2-O4A	1.931(4)	1.921(10)
M2-O4s	2.425(2)	2.478(10)
M2-O4sA	—	2.395(8)
S-O1s	1.473(2)	1.469(8)
S-O1sA	—	1.484(6)
S-O2s	1.488(2)	1.480(9)
S-O2sA	—	1.487(6)
S-O3s	1.476(2)	1.473(8)
S-O3sA	—	1.478(6)
S-O4s	1.476(2)	1.458(9)
S-O4sA	—	1.478(6)

bonds. The apical M2-O_{ap} bond lengths in the structure (II) (2.418(4)Å) is shorter than that in the structure (I) (2.425(2)Å) as well as in the structure of pure chalcathite (2.43 Å).⁷ It is explained by greater site occupation of the Fe atom.

Apical M2-O distances of 2.425(2)Å (I) and 2.418(4)Å (II) most likely refer to apical Cu-O bonds rather than Fe-O bonds. These values are more than the sum of ionic radii of the Fe²⁺ cation (0.92 Å, high spin, c.n. 6) and O²⁻ (c.n. 4) (1.24 Å). In the melantherite, FeSO₄·7H₂O, the Fe²⁺ cation is coordinated by six water molecule with an average Fe-O(W) distance of 2.116(3)Å.⁸ The coordination environment of the Fe2 atom becomes square-planar with the Fe2-O(water) bond lengths in the range of 1.97(1) - 2.03(1)Å in both structures.

The O atoms of the disordered aqua ligands surrounding the Cu2 atom have occupation factors of 0.42(4)/0.58(4) and 0.47(2)/0.53(2) for structure (I), and, 0.50(7)/0.50(7) and 0.7(1)/0.3(1) for structure (II).

The performed structural studies show that the substitution of iron for copper in chalcathite leads to disordering of the position of aqua ligands surrounding the M2 position and O atoms of the sulfate ion also breaking of the polymer chain at the Fe atom.

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