Role of Iron in Synthetic Tetrahedrites Revisited

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Abstract

The valence state of iron in $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$ tetrahedrites have been revisited by the combination of the crystallographic results, Mössbauer spectroscopy, and magnetization measurements. The crystal structure solution for $\text{Cu}_{11.0}\text{Fe}_{1.0}\text{Sb}_4\text{S}_{13}$ (space group $I\bar{4}3m$, $a = 10.3253(12)$, $z = 2$, $R = 0.011$) proved that iron substitutes for copper only in the Cu1 position. At the iron content of $x = 0.8$, 1.0, and 1.2, the presence of two nonequivalent and non-interacting Fe^{3+} cations was inferred from Mössbauer spectra. At higher levels of substitution ($x = 1.5$ and 2.0), room-temperature Mössbauer spectra indicate the electron hopping between part of Fe^{3+} and Fe^{2+} centers, whereas the rest of iron atoms exists as valence-localized Fe^{3+} and Fe^{2+} cations. Electron transfer is frozen out at 77 K, where a combination of two Fe^{3+} sites and one high-spin Fe^{2+} site is observed. Paramagnetic effective moments extracted from the magnetic susceptibility data point at the Fe^{3+} state of iron at $x = 0.8$, while a mixture of Fe^{2+} and Fe^{3+} is presumed in the samples with higher Fe content.

Keywords: tetrahedrite, iron, crystal structure, Mössbauer spectroscopy, electron hopping

1. Introduction

As the efficiency of current state-of-art thermoelectric materials has reached its limit, new ideas for the pursuit of better thermoelectrics are emerging. Thus, the families of semiconductors and semimetals based on complex tellurides, skutterudites, clathrates and various nanostructured materials were intensively investigated, bringing about new and exciting compounds with remarkable thermoelectric properties [1-4]. The unexpected discovery of high thermoelectric efficiency in synthetic and natural tetrahedrites opened a new direction in the search for thermoelectric materials of new generation [5, 6]. Tetrahedrites are a family of compounds with a general formula $\text{Cu}_{12-x}\text{M}_x\text{Sb}_4\text{S}_{13}$ ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Mn}, \text{Zn}$). They are easy to fabricate, do not contain toxic or rare elements, and their dimensionless thermoelectric figure-of-merit, ZT , reaches a value of 1.13 within the mid-temperature range [7]. Combined, the latter properties make tetrahedrites excellent candidates for creation of thermoelectric materials for automotive power generation [7-9].

Tetrahedrites containing Mn or Fe display the highest figure-of-merit [7], although the valence state of the substituting cation in these materials is different. It was demonstrated that iron is distinct from the other dopants. Whereas all other substituting $3d$ metals, including manganese, form the M^{2+} cations, the oxidation state of iron depends on the level of substitution [10]. It is generally believed [8, 10, 11] that in the $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$ series, Fe^{3+} forms until x reaches 1, while Fe^{3+} and Fe^{2+} coexist up to the maximum doping level of $x = 2$, at which Fe^{2+} is present exclusively. According to this model, one assumes that the parent compound $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, formulated as $(\text{Cu}^+)_{10}(\text{Cu}^{2+})_2(\text{Sb}^{3+})_4(\text{S}^{2-})_{13}$, transforms into $(\text{Cu}^+)_{11}(\text{Cu}^{2+})_1(\text{Sb}^{3+})_4(\text{S}^{2-})_{13}$ upon substitution of one iron atom for copper with a concomitant change in the oxidation state of one copper atom from +2 to +1. Further substitution of iron for copper leads to a decrease in the number of Fe^{3+} atoms and appearance of Fe^{2+} . For instance, at $x = 1.5$ the formula reads as $(\text{Cu}^+)_{10.5}(\text{Fe}^{3+})_{0.5}(\text{Fe}^{2+})_1(\text{Sb}^{3+})_4(\text{S}^{2-})_{13}$. Finally, at $x = 2$ only Fe^{2+} exists suggesting $(\text{Cu}^+)_{10}(\text{Fe}^{2+})_2(\text{Sb}^{3+})_4(\text{S}^{2-})_{13}$ formulation. The analysis of the literature data on the crystal structure and various properties of pristine and Fe-substituted tetrahedrites [8-16] makes us believe that the above description is unrealistic or, at least, oversimplified. In particular, the cubic unit cell parameter increases linearly with iron content, though Fe^{3+} is smaller than copper for which it substitutes [8, 9], and the hyperfine parameters of Mössbauer spectra do not match well with the values expected for high-spin iron tetrahedrally coordinated by sulfur atoms [10, 11]. Taking these considerations into account, we have undertaken a comprehensive study of Fe-substituted tetrahedrites by means of X-ray

crystallography, Mössbauer spectroscopy, and magnetization measurements in order to re-examine the role and the valence state of iron in the $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$ compounds.

In this paper, we present the results of the complex study of iron-substituted tetrahedrites $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$ as well as discuss the role of iron and the relevance of the proposed distribution of the oxidation states in $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$. We also put forward new, hitherto unexplained properties of these materials.

2. Experimental

2.1. Starting materials

Elemental Fe (powder, 99 %), Sb (pieces, 99.999 %), CuO (99.9 %), and elemental S were used as starting materials for the synthesis. Copper was obtained by heating CuO under hydrogen flow. Sulfur was gently heated slightly above its melting point under dynamic vacuum for complete water removal. The purity of all reagents was controlled by powder X-ray diffraction.

2.2. Synthesis

$\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$ ($x = 0, 0.5, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.5, \text{ and } 2.0$) compounds were prepared by a standard ampoule technique generally following the procedure described in the literature [5]. In brief, the mixtures of starting materials were sealed in evacuated quartz ampoules under a vacuum of 2×10^{-2} Torr. Ampoules were heated to 973 K, annealed at this temperature for 3 h, slowly cooled down to 823 K in 30 h, and finally cooled down to room temperature in a switched-off furnace. The reaction products were finely ground in agate mortar and pressed into pellets at a pressure of 80-100 bar at room temperature. These pellets were sealed in evacuated quartz ampoules and annealed at 773 K for 25 h, followed by switching off the furnace and cooling down to room temperature. For each composition, 3 to 5 samples were synthesized in parallel experiments under the same conditions to ensure reproducibility. The resulting samples were finely ground and used for further investigations.

2.3. X-ray Powder Diffraction and Energy-Dispersive X-ray Spectroscopy

Phase composition was investigated by a standard X-ray technique using a STADI-P powder diffractometer (Stoe, Cu $K_{\alpha 1}$ radiation, Ge monochromator, $\lambda = 1.540598 \text{ \AA}$). The program package STOE WinXPOW was used for data processing. Unit cell parameters for each composition were calculated for 3-5 different synthetic batches and averaged. Elemental composition was determined using a JSM JEOL scanning electron microscope operated at 30 kV and equipped with an EDX detection system INCA x-Sight. Pure elemental Co was used as a standard. The data were collected from 10 points for each sample and then averaged.

Uniform distribution of elements across the sample was confirmed by mapping (see *Supporting Information*, Figure S1).

2.4. Crystal Structure Investigation

A suitable single crystal was selected from the product of the first annealing step of the composition $\text{Cu}_{11.0}\text{Fe}_{1.0}\text{Sb}_4\text{S}_{13}$. Data were collected at 100 K on a Bruker D8 VENTURE with PHOTON 100 CMOS detector system equipped with a Mo-target X-ray tube. A frame width of 0.50° and an exposure time of 15 s/frame were employed for data collection. Data reduction and integration were performed with the Bruker software package SAINT. Data were corrected for absorption effects using the empirical methods (multi-scan) as implemented in SADABS. The structure was solved and refined using SHELXTL programs. Direct methods were used to solve the crystal structure in the space group $I\bar{4}3m$ (No. 217) in accordance with the literature data [15]. The crystal structure was refined with anisotropic thermal parameters for all atoms, which resulted in $R = 0.011$. Data collection and refinement parameters are listed in Table 1, atomic parameters in Table 2, and interatomic distances and bond angles in Table 3. Details of the crystal structure refinement are given and discussed in the Results and Discussion section.

2.5. Mössbauer spectroscopy

^{57}Fe Mössbauer spectra were recorded at 77 and 300 K using a conventional constant-acceleration spectrometer MS-1104Em in the transmission geometry. A radiation source $^{57}\text{Co}(\text{Rh})$ was kept at room temperature. All isomer shifts are referred to $\alpha\text{-Fe}$ at 298 K. Experimental spectra were processed and analyzed using methods of spectral simulations implemented in the SpectrRelax program [17].

2.6. Magnetic properties

Magnetization was measured with the VSM setup of the Physical Property Measurement System (PPMS, Quantum Design) in external magnetic fields of 0.1, 1, 2 and 5 T in the temperature range from 2 to 380 K, using pellets prepared by pressing finely ground polycrystalline samples at a pressure of 80-100 bar at room temperature.

3. Results and discussion

3.1. Synthesis and homogeneity range

Powder XRD patterns for all obtained samples can be indexed in a cubic body-centered lattice with the unit cell parameters a ranging from 10.320 to 10.378 Å. Careful inspection of the patterns showed that at low ($x = 0$ and 0.5) and high ($x = 1.5$ and 2.0) iron content peaks of a secondary phase Cu_3SbS_4 appear reproducibly (see *Supporting Information*, Figure S2). This observation agrees well with the previous work by Tatsuka and

Marimoto [18]. They investigated phase relations in the quaternary Cu-Fe-Sb-S system and found that for $x = 0\text{--}0.5$ the stoichiometric compositions do not belong to the homogeneity range of tetrahedrite. Instead, tetrahedrite coexists with Cu_3SbS_4 at these iron concentrations. For $x = 1.5\text{--}2.0$, the same authors also observed certain deviations from the stoichiometric composition and proposed that not only Cu_3SbS_4 , but also Cu_5FeS_4 appears as a side product. The latter compound was not observed in our work, though. As the amount of Cu_3SbS_4 impurity exceeds 3 wt% for the samples with $x = 0$ and 2.0, we do not consider their unit cell parameters reliable, and therefore show only the unit cell parameters for compounds with $x = 0.5\text{--}1.5$ in Figure 1. The cubic unit cell parameter linearly increases with increasing x , in good agreement with the literature data, but contradicting the change in the ionic radii upon substitution of Fe for Cu, provided that the 3+ state is assumed for iron according to the literature data for all compositions with $x \leq 1.0$ [8, 10]. Indeed, if Cu^{2+} is replaced by Fe^{3+} , a decrease in the unit cell parameter by more than 10% is expected from the comparison of the ionic radii for the high-spin state in the tetrahedral coordination: Cu^+ , 0.60 Å; Cu^{2+} , 0.57 Å; Fe^{2+} , 0.63 Å; and Fe^{3+} , 0.49 Å [19].

3.2. Crystal structure refinement and description

The solution of the crystal structure by direct methods revealed five positions in the space group $I\bar{4}3m$ occupied by copper, antimony, and sulfur, *viz.* Cu1 in 12*d*, Cu2 in 12*e*, Sb in 8*c*, S1 in 24*g* and S2 in 2*a*. The analysis of the atomic displacement parameters (ADP's) enabled us to notice two important features. First, the Cu1 atom, which has a tetrahedral environment of sulfur atoms, displays a rather high ADP. Consequently, this position was refined assuming mixed occupancy by iron and copper, which reduced the ADP to reasonable values. Second, the Cu2 atom, which resides in the center of a sulfur triangle, exhibits a significantly elongated displacement ellipsoid oriented perpendicular to the triangular plane. A careful inspection of the difference Fourier map revealed that the Cu2 position is split and thus better described by an atom in the 24*g* site with 50% occupancy. At the later stages of refinement, the occupancy factors for antimony and sulfur atoms were refined and converged to exactly 100% each. After that, the Cu:Fe ratio was refined for the Cu1 position and converged to 81(2):19(2). It was further fixed at 83:17 according to the experimental composition. Finally, the crystal structure was refined in an anisotropic approximation leading to $R = 0.011$ and to the atomic parameters listed in Table 2.

A view of the crystal structure of $\text{Cu}_{11}\text{FeSb}_4\text{S}_{13}$ is given in Figure 2. It is based on a three-dimensional framework composed of $[\text{Cu1/Fe1}(\text{S1})_4]$ tetrahedra that share all vertices. This framework contains cavities hosting the $[\text{Cu2}(\text{S1})_2\text{S2}]$ and $[\text{Sb}(\text{S1})_3]$ pyramidal units.

These units are centered at the S2 atom forming a cluster depicted in Figure 3. Since the Cu2 atom does not sit in the plane of the sulfur triangle, it moves closer to the Sb atom to achieve the Cu2–Sb distance of 3.17 Å. Furthermore, the separation between the two neighboring Cu2 sites is only 0.47 Å, which indicates that only one of the neighboring positions is occupied, and the occupied and vacant positions alternate within a cluster in one out of four possible regular ways, as shown in Figure 3. However, such an alternation is local and does not result in any visible superstructure. Consequently, the Sb atom may form up to three bonds with the Cu2 atoms, and the probability that a given antimony atom does not form Sb–Cu2 bonds is only 1/8. Therefore, the description of the [Sb(S1)₃] unit as a pyramid with an Sb³⁺ atom bearing a stereochemically active lone pair is generally incorrect. Rather, for the majority of the Sb atoms this lone pair is involved in interaction with the Cu2 atoms, similar to the situation previously observed for Sn²⁺ cations in cationic clathrates [20].

Given the high accuracy of the crystal structure refinement, we conclude that iron mixes with copper only at the Cu1 site, which agrees perfectly with the neutron diffraction data of Andreasen et al. [14] and consents with the propensity of iron to have the tetrahedral coordination in various sulfides [21]. The splitting of the Cu2 atomic position results in the formation of Sb–Cu2 bonds, in full agreement with the literature data [9, 12]. Moreover, the alternation of occupied and vacant Cu2 positions within a cluster centered at the S2 atom may well lead to a random sequence of clusters, where all Sb atoms form from one to three bonds with the Cu2 atoms, and those clusters where Sb atoms have the stereoactive lone pair. We also note that the Cu2 atom in the 24g position retains a slightly elongated displacement ellipsoid pointing towards the [S₃] triangle plane. This effect was previously noticed in the literature for pristine [12] and Mn-substituted tetrahedrites [9]. For these compounds, two scenarios were proposed – the anharmonic displacement or rattling of the Cu2 atoms, both effects being responsible for low thermal conductivity observed experimentally. Finally, all positions except that of Cu2 are fully occupied, thus leaving no space for vacancies.

3.3. Mössbauer spectroscopy

⁵⁷Fe Mössbauer spectra were recorded for the samples with $x = 0.8, 1.0, 1.2, 1.5$, and 2.0. First four samples were chosen as they belong to the homogeneity range of the Fe-bearing tetrahedrite [18] and were proved to be phase-pure. The latter sample was included as a reference to follow the development of the hyperfine parameters and their intensities. Though this sample was not phase-pure, it was not contaminated by any Fe-contained impurities.

The ⁵⁷Fe Mössbauer spectra of all Cu_{12-x}Fe_xSb₄S₁₃ compositions acquired in this work at 300 K can be subdivided into two groups. The first group comprises spectra for the samples

with $x = 0.8, 1.0$, and 1.2 (Figure 4). Each of those can be described as a superposition of two quadrupole doublets, Fe1 and Fe2, characterized by different values of isomer shifts δ and quadrupole splitting Δ , thus corresponding to two types of iron atoms. The minor component Fe1, which provides about 15% of the spectral area, exhibits the average values of the isomer shift, $\langle \delta_1 \rangle \approx 0.17$ mm/s, expected for the high-spin Fe^{3+} cation in environment of sulfur atoms, though its quadrupole splitting $\langle \Delta_1 \rangle \approx 0.69$ mm/s (Table 4) is quite high for the symmetric sulfur coordination [11, 21]. At the same time, the major Fe2 component of the spectra ($I_2 \approx 85\%$) has a noticeably larger isomer shift than typically observed for Fe^{3+} sulfides (0.15-0.25 mm/s), whereas its quadrupole splitting is typical for the high-spin Fe^{3+} in symmetric tetrahedral environment [11, 22]. Although the hyperfine parameters for both components of the spectra could be crudely ascribed to Fe^{3+} , we note that these parameters are not typical for the high-spin Fe^{3+} in symmetrical tetrahedral environment of four sulfur atoms. We also note that the spectrum acquired at 77 K for the compound with $x = 1$ (not shown) shows virtually no changes in the line shape and hyperfine parameters compared to those observed at 300 K.

Therefore, we conclude that first, no sign of Fe^{2+} is observed up to the composition $x = 1.2$, in contradiction with the accepted model of the charge distribution (see Introduction for details), according to which 20% of iron atoms should be in the Fe^{2+} state at $x = 1.2$ and thus should be easily detectable by this method. Second, the coexistence of two components of the spectra observed in our work has never been reported in the literature. For instance, Makovicky et al. described the spectrum of $\text{Cu}_{11}\text{Fe}_1\text{Sb}_4\text{S}_{13}$ as a single quadrupole doublet with $\delta = 0.31$ mm/s and $\Delta = 0.29$ mm/s [10], which might be explained by a low signal intensity. We note that the crystallographic data obtained in this work and those reported in the literature [14] explicitly indicate that iron occupies only one crystallographic position, partially substituting Cu1. Therefore, the appearance of two quadrupole doublets stems from the local nonequivalence of iron. Pairing of iron centers through a sulfur bridge, clusterization of Fe atoms, or their selected interaction with copper atoms are likely reasons for such nonequivalence. We should stress that the intensity of Fe1 quadrupole doublet for all three compounds is more than 15%, which is too large to be associated with the presence of an X-ray undetected Fe-contained side phase. In addition, hyperfine parameters of this quadrupole doublet for all compositions are the same, thus, we cannot link it with the presence of the impurity. Therefore, we conclude that the observed spectra represent intrinsic properties of the studied compositions.

The ^{57}Fe Mössbauer spectra of $\text{Cu}_{10.5}\text{Fe}_{1.5}\text{Sb}_4\text{S}_{13}$ and $\text{Cu}_{10}\text{Fe}_2\text{Sb}_4\text{S}_{13}$ at 300 K are considerably more complex (Figure 5) and can be roughly described as a superposition of three quadrupole doublets Fe1, Fe2 and Fe3. The hyperfine parameters of the Fe1 and Fe2 doublets (Table 5) are close to those for the samples $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$ with $x = 0.8, 1.0$, and 1.2 . Both Fe2 and Fe3 doublets have very broad components. Such a broadening can be related to the relaxation effects due to electron hopping [11]. The relaxation process is most obvious in the case of $\text{Cu}_{10.5}\text{Fe}_{1.5}\text{Sb}_4\text{S}_{13}$ (Figure 5), where the Fe2 doublet and one of the Fe3 lines are not well resolved, and a continuous absorption appears between the right-hand Fe2 ($\nu_2 \approx 0.6$ mm/s) and Fe3 ($\nu_3 \approx 2.2$ mm/s) peaks (see Figure 5). The fact that the continuous absorption is the strongest for $\text{Cu}_{10.5}\text{Fe}_{1.5}\text{Sb}_4\text{S}_{13}$, where the amounts of Fe^{3+} and Fe^{2+} are comparable, indicates that this effect must arise from the electron exchange between the Fe^{2+} and Fe^{3+} ions. Apparently, this exchange is a thermally activated process, as deduced from the disappearance of the continuous absorption upon decreasing the temperature. Indeed, the spectra of both samples at $T = 77$ K can be described as a superposition of three "discrete" quadrupole doublets (Figure 6) corresponding to the Fe^{3+} ions (Fe1 and Fe2) and the high-spin divalent Fe^{2+} ions (Fe3) with hyperfine parameters summarized in Table 6. The profile of Mössbauer spectra for two Fe^{2+} and Fe^{3+} charge states is expected to be very sensitive to the difference between their resonance frequencies ($\omega_{\text{Fe3}} - \omega_{\text{Fe2}} \approx 10^8 \text{ s}^{-1}$, which corresponds to $(\nu_3 - \nu_2) \approx 1.6$ mm/s (see Figure 6) and the electron hopping frequency (ω_{hop}) for the $\text{Fe}_a^{2+} - \text{Fe}_b^{3+} \leftrightarrow \text{Fe}_a^{3+} - \text{Fe}_b^{2+}$ reaction. If $\omega_{\text{hop}} \ll 10^8 \text{ s}^{-1}$, the Mössbauer spectra are a superposition of individual Fe^{2+} and Fe^{3+} subspectra, as observed at 77 K. With increasing temperature, the value of ω_{hop} increases, and in a region of ω_{hop} around 10^8 s^{-1} , a strong line broadening leads to the absorption in the entire region extending between the Fe^{2+} and Fe^{3+} lines as observed at 300 K (Figure 5). Further increase of ω_{hop} ($> 10^8 \text{ s}^{-1}$) is expected to result in a merge of this broad absorption region into one "mixed" $\text{Fe}^{2.5+}$ line with weighted average parameters (δ, Δ) of the Fe^{2+} and Fe^{3+} subspectra [22, 23].

In order to analyze the experimental Mössbauer spectra taking into account the above relaxation processes, we used a stochastic model given by *Tjon* and *Blume* [24] for the description of a spectrum in the presence of stochastic hyperfine fluctuations. Following their procedure, we attempted to simulate the Mössbauer spectra of the $\text{Cu}_{10.5}\text{Fe}_{1.5}\text{Sb}_4\text{S}_{13}$ and $\text{Cu}_{10}\text{Fe}_2\text{Sb}_4\text{S}_{13}$ samples using the two-level relaxation processes between $(\text{Fe}_a^{2+} - \text{Fe}_b^{3+})_1 \leftrightarrow (\text{Fe}_a^{3+} - \text{Fe}_b^{2+})_2$ nuclear energy levels with a relaxation time $\tau = (\omega_{\text{hop}})^{-1}$ given by $\tau = (\tau_{12} \tau_{21}) / (\tau_{12} + \tau_{21})$, where τ_{12} and τ_{21} stand for the relaxation times for "1" to "2" and for "2" to

“1” states, respectively. The relative probability for the $(\text{Fe}_a^{2+}-\text{Fe}_b^{3+})_1$ state is given by $n_1 = \tau/\tau_{21}$. It is necessary to assume opposite signs for the quadrupole interaction in the Fe^{2+} and Fe^{3+} sites and to leave the values of isomer shift and quadrupole splitting as variables. Thus, four parameters $\{\delta_i, \Delta_i\}_{i=2,3}$ for both iron states, the relaxation time τ (or the hopping frequency ω_{hop}), and the ratio of probabilities $n_1/n_2 = \omega_{21}/\omega_{12}$ are to be determined to interpret the Mössbauer spectra shown in Figure 5 (the minimum experimental line width W was constrained for all the doublets to 0.25 mm/s). The simulated results are represented by solid lines in Figure 5 and fitting parameters are listed in Table 5.

Comparison of the fitting results at two temperatures (Tables 5 and 6) shows that no additional resonances with temperature-dependent hyperfine parameters as well as no line broadenings, except those which are caused by relaxation, had to be introduced in order to yield satisfactory fits to the experimental data. The isomer shifts δ_2 and δ_3 show a slight decrease with increasing temperature, as expected from the variation of the second-order Doppler shift [25]. In addition, a slight decrease of the quadrupole splitting Δ_3 for the Fe^{2+} sites with increasing temperature is typical of a valence-contribution-dominated electric field gradient with a temperature dependence determined by the Boltzmann population of the orbital states split by the crystal field. Therefore, our data demonstrate that the Fe^{3+} ions are involved in the electron hopping with a part of the Fe^{2+} ions, but no additional change of electron configuration of iron atoms occurs upon changing the temperature.

Within the above model, the best description of the spectra for the compounds with $x = 1.5$ and 2.0 measured at 300 K (Figure 5) may be obtained only by taking into account a superposition of individual Fe2 and Fe3 components (valence-localized states) along with the continuous absorption (relaxing state), thus implying that the electron exchange process occurs just for part of the Fe^{3+} and Fe^{2+} pairs. We attribute the latter to a non-equivalence of the $\text{Fe}_a^{3+/2+}$ and $\text{Fe}_b^{3+/2+}$ sites, which is expected from the presence of different cations (Cu^+ , Sb^{3+} , Fe^{2+}) in their local environments. This non-equivalence also manifests itself in the line broadening observed in the Fe2 pattern for the $\text{Cu}_{10}\text{Fe}_2\text{Sb}_4\text{S}_{13}$ sample at 77 K (Table 6). This non-equivalence can be represented by a difference U_0 between a pair of two sublevels “1” and “2” (Figure 7). Within the model of a double potential [22], assuming that the electron exchange takes place mainly in isolated Fe^{2+} and Fe^{3+} pairs, the relevant parameters are the potential well difference U_0 and the intervening potential barrier E_A (Figure 7) representing the self-trapping energy due to the local lattice deformation and electrical polarization [23, 24]. According to this simple model, the number of electron jumps $(\text{Fe}_a^{2+}-\text{Fe}_b^{3+})_1 \leftrightarrow (\text{Fe}_a^{3+}-\text{Fe}_b^{2+})_2$ from the lower level (“1”) to the upper one (“2”) is proportional to the thermal fraction

having sufficient energy to pass the barrier ($U_0 + E_A$) [22]: $\omega_{hop} \propto \exp\{-(U_0 + E_A)/kT\}$. Upon temperature increase, the condition $\omega_{hop} \approx 10^8 \text{ s}^{-1}$ is satisfied for increasing energy U_0 and the number of $\text{Fe}^{2+}/\text{Fe}^{3+}$ pairs that produce “mixed” spectra with the positions determined by the population fraction, $n_2 \propto \exp\{-U_0/kT\}$, of the energetically unfavorable site determined by the U_0 value. This shows that the observation of the continuous absorption finds a natural explanation in the small ΔU (ΔU^*) distribution (Figure 7) due to the nonequivalence of iron sites. Interestingly, the width of this distribution, which reflects the degree of perturbation of the electron delocalization, depends on the stoichiometry of the sample.

For a more detailed analysis of the relaxation parameters, the extensive temperature-dependent ^{57}Fe Mössbauer measurements for the samples $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$ with $1 < x \leq 2$ are required. Analysis of such measurements is beyond the scope of this work.

3.4. Magnetic properties

To the best of our knowledge, no information on magnetic properties of the Fe-substituted tetrahedrite is available in the literature. In the only parent tetrahedrite studied, a combination of magnetic susceptibility measurements and ESR spectroscopy results confirmed the presence of Cu^{2+} [26]. However, magnetization data could effectively complement Mössbauer spectra in regard to the valence states of iron. This information is especially important for the samples with lower doping levels, where spectral parameters are somewhat different from those of the reference Fe^{3+} materials. Figure 8 shows reciprocal magnetic susceptibility of $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$ ($x = 0.8, 1.0, 1.2$) plotted as a function of temperature. The $1/\chi(T)$ dependence reveals Curie-Weiss paramagnetic behavior, and no field dependence is observed. Using the modified Curie-Weiss law $\chi = \chi_0 + C_{CW}/(T + \theta_{CW})$, temperature-independent susceptibility χ_0 , Curie-Weiss temperature θ_{CW} , and Curie-Weiss constant C_{CW} for each compound were calculated using the 5 T data, and the effective paramagnetic moments per one iron atom were obtained.

The χ_0 susceptibility is defined as: $\chi_0 = \chi_P + \chi_{\text{core}} + \chi_{\text{VV}} + \chi_L$, where χ_P is the Pauli paramagnetic spin susceptibility of conduction electrons, χ_{core} is the diamagnetic orbital contribution from the core electrons, χ_{VV} is the Van Vleck paramagnetic orbital contribution, and χ_L is the Landau orbital diamagnetism of the conduction electrons. Taking into account that iron-substituted tetrahedrites demonstrate semiconducting properties, χ_0 is mainly determined by χ_{core} . The values extracted from the experimental data, $\chi_0 = -7 \cdot 10^{-4}$, $-3 \cdot 10^{-4}$, and $-5 \cdot 10^{-4} \text{ emu/mol}$ for $x = 0.8, 1.0$ and 1.2 , respectively, are in agreement with the χ_{core} value calculated from the literature data [27]: χ_{core} is $-6 \cdot 10^{-4} \text{ emu/mol}$ for all investigated samples (the deviation from this value for different compounds is suppressed by rounding

because of low difference in the iron content). The negative values of the Curie-Weiss temperature, $\theta_{CW} = -30.9, -36.5,$ and -36.6 K for $x = 0.8, 1.0,$ and $1.2,$ respectively, indicate dominant antiferromagnetic interactions between the iron spins for all investigated compounds. Effective paramagnetic moments are $5.87, 5.67,$ and $5.55 \mu_B/\text{Fe}$ for $x = 0.8, 1.0,$ and $1.2,$ respectively. Therefore, only Fe^{3+} with the spin-only effective moment of $5.92 \mu_B$ ($S = 5/2$) is present in the sample with $x = 0.8$. The lower effective moments for the samples with higher Fe content imply the mixing of Fe^{2+} and Fe^{3+} .

We conclude that the magnetic moment per Fe atom changes with nearly the same increment upon going from $x = 0.8$ to $x = 1.0$ and to $x = 1.2$. No abrupt drop of the moment occurs upon crossing the $x = 1.0$ value, where, according to the literature (see Introduction), a transition from pure Fe^{3+} to coexisting Fe^{3+} and Fe^{2+} is expected. However, the putative coexistence of Fe^{2+} and Fe^{3+} at $x = 1.0$ and $x = 1.2$ is at odds with the Mössbauer data, where both spectral lines can be ascribed to Fe^{3+} . The origin of this discrepancy is not clear at the moment and requires further investigation.

For comparison, Figure 8 also displays the temperature dependence of reciprocal magnetic susceptibility for the sample with $x = 1.5$ at 5 T external field. While the susceptibility seemingly follows the modified Curie-Weiss law, it demonstrates a strong field dependence (not shown), which was not observed for $x = 0.8, 1.0,$ and 1.2 . This may originate in the charge transfer between the iron centers and will be a topic of a separate study.

4. Conclusions

Combining the structural data with the results of Mössbauer spectroscopy and magnetization measurements, we propose that the literature model for the Fe^{3+} and Fe^{2+} distribution in iron-containing tetrahedrites $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$ should be amended. The analysis of the crystal structure confirms that iron substitutes copper only in one position, Cu1, but the Mössbauer spectra provide evidence for two locally nonequivalent iron atoms for all compositions from $x = 0.8$ to $x = 2.0$. Furthermore, the Mössbauer data suggest that two ranges of Fe doping level exist. The first one includes $x = 1.5$ and $x = 2.0$ and can be described by a model assuming electron hopping between the Fe^{3+} and Fe^{2+} centers, which freezes out upon cooling down to 77 K. Importantly, such electron hopping takes place between a part of iron centers only, whereas the rest of iron atoms exists as localized Fe^{3+} and Fe^{2+} cations. For the compositions with lower iron content, $x = 0.8, 1.0,$ and $1.2,$ two nonequivalent Fe^{3+} cations manifest themselves in Mössbauer spectra. Those iron centers do not interact with each other; however, the results of the magnetization measurements suggest that the effective moment per one iron center is somewhat lower than required by a high-spin

Fe^{3+} cation. Apparently, an interaction between Fe^{3+} and copper centers cannot be ruled out, but for $x = 1.2$ composition the electroneutrality cannot be achieved by combining only Fe^{3+} and Cu^+ ; therefore, other explanations should be put forward to account for unusual behavior of iron-bearing tetrahedrites. This is important in light of their thermoelectric properties, especially since the recent report [28] argues that strong coupling of charge carriers and doped spins is accountable for high thermoelectric efficiency of *d*-metal chalcogenides. Further study of the electronic structure and electron correlations in synthetic tetrahedrites is currently underway.

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References

1. M.G. Kanatzidis, Structural Evolution and Phase Homologies for “Design” and Prediction of Solid-State Compounds, *Acc. Chem. Res.* 38 (2005) 359–368.
2. Y. Dong, P. Puneet, T.M. Tritt, G.S.Nolas, Crystal structure and high temperature transport properties of Yb-filled p-type skutterudites $\text{Yb}_x\text{Co}_{2.5}\text{Fe}_{1.5}\text{Sb}_{12}$, *J. Solid State Chem.* 209 (2014) 1–5.
3. L.D. Zhao, S.H. Lo, Y. Zhang, H. Sun, G. Tan, C. Uher, C. Wolverton, V. P. Dravid, M.G. Kanatzidis, Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals, *Nature* 508 (2014) 373–377.
4. A.V. Shevelkov, K. Kovnir, Zintl Clathrates, *Struct. Bond.* 139 (2011) 97–142.
5. K. Suekuni, K. Tsuruta, M. Kunii, H. Nishiate, E. Nishibori, S. Maki, M. Ohta, A. Yamamoto, M. Koyano, High-performance thermoelectric mineral $\text{Cu}_{12-x}\text{Ni}_x\text{Sb}_4\text{S}_{13}$ tetrahedrite, *J. Appl. Phys.* 113 (2013) 043712.
6. X. Lu, D.T. Morelli, Y. Xia, F. Zhou, V. Ozolins, H. Chi, X. Zhou, C. Uher, High performance thermoelectricity in earth-abundant compounds based on natural mineral tetrahedrites, *Adv. Energy Mater.* 3 (2013) 342–348.
7. J. Heo, G. Laurita, S. Muir, M.A. Subramanian, D.A. Keszler, Enhanced thermoelectric performance of synthetic tetrahedrites, *Chem. Mater.* 26 (2014) 2047–2051.
8. K. Suekuni, Y. Tomizawa, T. Ozaki, M. Koyano, Systematic study of electronic and magnetic properties for $\text{Cu}_{12-x}\text{TM}_x\text{Sb}_4\text{S}_{13}$ (TM = Mn, Fe, Co, Ni, and Zn) tetrahedrite, *J. Appl. Phys.* 115 (2014) 143702.
9. R. Chetty, P. Kumar, G. Rogl, P. Rogl, E. Bauer, H. Michor, S. Suwas, S. Puchegger, G. Giester, R.C. Mallik, Thermoelectric properties of a Mn substituted synthetic tetrahedrite, *Phys. Chem. Chem. Phys.* 17 (2015) 1716–1727.
10. E. Macovicky, K. Forcher, W. Lottermoser, G. Amthauer, The role of Fe^{2+} and Fe^{3+} in synthetic Fe-substituted tetrahedrite, *Miner. Petrol.* 43 (1990) 73–81.
11. E. Macovicky, G. Tippet, K. Forcher, W. Lottermoser, S. Karup-Møller, G. Amthauer, Mössbauer study of Fe-bearing synthetic tennantite, *Can. Mineral.* 41 (2003) 1125–1134.
12. A. Pfitzner, M. Evain, V. Petriček, $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$: a temperature-dependent structure investigation, *Acta Cryst. B* 53 (1997) 337–345.
13. N.E. Johnson, J.R. Craig, J.D. Rimstidt, Crystal chemistry of tetrahedrite, *Am. Mineral.* 73 (1988) 389–397.

14. J.W. Andreasen, E. Macovicky, B. Lebech, S. Karup-Møller, The role of iron in tetrahedrite and tennantite determined by Rietveld refinement of neutron powder diffraction data, *Phys. Chem. Minerals* 35 (2008) 447–454.
15. K. Friese, A. Grzechnik, E. Macovicky, T. Balic-Zunic, S. Karup-Møller, Crystal structures of iron bearing tetrahedrite and tennantite at 25 and 250°C by means of Rietveld refinement of synchrotron data, *Phys. Chem. Minerals* 35 (2008) 455–465.
16. B.J. Wuensch, The crystal structure of tetrahedrite, $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, *Z. Kristallogr* 119 (1964) 437–453.
17. M.E. Matsnev, V.S. Rusakov, An Application for Mössbauer Spectra Modeling and Fitting, *AIP Conf. Proc.* 1489 (2012), 178–185.
18. K. Tatsuka, N. Morimoto, Tetrahedrite stability relations in the Cu-Fe-Sb-S system, *Am. Mineral.* 62 (1977) 1101–1109.
19. R. Dronskowski, *Computational Chemistry of Solid State Materials*. Wiley-VCH. Weinheim (2005) 294 p.
20. K.A. Kovnir, A.V. Sobolev, I.A. Presniakov, O.I. Lebedev, G. Van Tendeloo, W. Schnelle, Yu. Grin, A.V. Shevelkov, $\text{Sn}_{19.3}\text{Cu}_{4.7}\text{As}_{22}\text{I}_8$: a New Clathrate-I Compound with Transition-Metal Atoms in the Cationic Framework, *Inorg. Chem.* 44 (2005) 8786–8793.
21. J.B. Goodenough, G.A. Fatseas, Mössbauer ^{57}Fe isomer shift as a measure of valence in mixed-valence iron sulfides, *J. Solid State Chem.* 41 (1982), 1–22.
22. C. Achim, E.L. Bominaar, R.J. Staples, E. Münck, R.H. Holm, Influence of Extrinsic Factors on Electron Transfer in a Mixed-Valence $\text{Fe}^{2+}/\text{Fe}^{3+}$ Complex: Experimental Results and Theoretical Considerations, *Inorg. Chem.* 40 (2001) 4389–4403.
23. D.A. Nolet, R.G. Burns, Ilvaite: a study of temperature dependent electron delocalization by the Mössbauer effect, *Phys. Chem. Minerals* 4 (1979) 221–234.
24. J.A. Tjon, M. Blume, Mössbauer Spectra in a Fluctuating Environment II. Randomly Varying Electric Field Gradients, *Phys. Rev.* 165 (1968) 456–461.
25. P. Gülich, E. Bill, A.X. Trautwein, *Mössbauer Spectroscopy and Transition Metal Chemistry (Fundamentals and Applications)*, Springer (2011).
26. F. Di Benedetto, G. P. Bernardini, C. Cipriani, C. Emiliani, D. Gatteschi, M. Romanelli, The distribution of Cu(II) and the magnetic properties of the synthetic analogue of tetrahedrite: $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, *Phys. Chem. Minerals* 32 (2005) 155–164.
27. G.A. Bain, J.F. Berry, Diamagnetic Corrections and Pascal's Constants, *J. Chem. Educ.* 85 (2008) 532–536.

28. R. Ang, A.U. Khan, N. Tsujii, K. Takai, R. Nakamura, T. Mori, Thermoelectricity Generation and Electron–Magnon Scattering in a Natural Chalcopyrite Mineral from a Deep-Sea Hydrothermal Vent, *Angew. Chem. Int. Ed.* 54 (2015) 12909–12913.

Table 1. Summary of data collection and refinement parameters for $\text{Cu}_{11.0}\text{Fe}_{1.0}\text{Sb}_4\text{S}_{13}$

Composition	$\text{Cu}_{11.0}\text{Fe}_{1.0}\text{Sb}_4\text{S}_{13}$
Crystal system	Cubic
Space Group	$I\bar{4}3m$
a , Å	10.3253(12)
V , Å ³	1100.8(4)
Z	1
d_{calc}	5.004
Radiation/wavelength	MoK α /0.71073Å
Temperature, K	100(2)
Crystal size, mm ³	0.12×0.09×0.06
Color	dark gray
Absorption correction	SADABS
θ range (data collection)	2.79 – 30.54
Range of h, k, l	-14 $\rightarrow h \rightarrow$ 14, -14 $\rightarrow k \rightarrow$ 14, -14 $\rightarrow l \rightarrow$ 14
R_{int}	0.0744
R/R_w ($I > 2\sigma(I)$)	0.0116/0.0238
Flack parameter x	-0.004(17)
GoF	1.205
Δr_{max} (e/Å ⁻³)	0.563/-0.324

Table 2. Atomic parameters in the crystal structure of $\text{Cu}_{11.0}\text{Fe}_{1.0}\text{Sb}_4\text{S}_{13}$

Atom	Wyckoff position	x	y	z	$U_{eq}, \text{\AA}^2$
Sb	$8c$	0.231111(13)	x	$-x$	0.01097(7)
Cu1/Fe1 ^{a)}	$12d$	1/4	1/2	0	0.00972(11)
Cu2	$24g$	0.01406(18)	x	0.78230(8)	0.0256(5)
S1	$24g$	0.38412(4)	x	0.86277(5)	0.00853(11)
S2	$2a$	0	0	0	0.0137(4)

^{a)} The Cu/Fe ratio is fixed at 0.83/0.17. See text for details.

Table 3. Interatomic distances and bond angles

Atom–Atom	Distance, Å	Atom–Atom–Atom	Angles, deg.
Sb–S1	2.4355(6)	S1–Sb1–S1	95.48(2)
Sb–Cu2	3.172(3)	S1–Cu1/Fe1–S1	110.977(12)
Cu1/Fe1–S1	2.3146(4)	S1–Cu1–S1	106.50(2)
Cu2–S1	2.2691(8)	S1–Cu2–S1	96.44(5)
Cu2–S2	2.2572(9)	S2–Cu2–S1	130.48(3)
Cu2–Cu2	2.974(3)		

Table 4. Parameters of the ^{57}Fe Mössbauer spectra for $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$ ($x = 0.8, 1.0, 1.2$) at 300 K

Sample	Subspectrum	δ [mm/s]	Δ [mm/s]	W [mm/s]*	I [%]
$\text{Cu}_{11.2}\text{Fe}_{0.8}\text{Sb}_4\text{S}_{13}$	Fe1	0.19(2)	0.72(3)	0.24	16(2)
	Fe2	0.31(1)	0.28(1)	0.24(2)	84(2)
$\text{Cu}_{11.0}\text{Fe}_{1.0}\text{Sb}_4\text{S}_{13}$	Fe1	0.17(1)	0.72(3)	0.26	15(2)
	Fe2	0.32(1)	0.28(1)	0.26(1)	85(2)
$\text{Cu}_{10.8}\text{Fe}_{1.2}\text{Sb}_4\text{S}_{13}$	Fe1	0.14(3)	0.63(3)	0.28	17(1)
	Fe2	0.32(2)	0.27(2)	0.28(1)	83(1)

(*) values of the relevant parameters were assumed to be equal to each other.

Table 5. Parameters of the ^{57}Fe Mössbauer spectra for $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$ ($x = 1.5, 2.0$) at 300 K

Sample	Subspectrum	δ [mm/s]	Δ [mm/s]	ω_{hop} [s^{-1}] $\times 10^7$	$n_{\text{Fe(II)}}/n_{\text{Fe(III)}}$	I [%]
$\text{Cu}_{10.5}\text{Fe}_{1.5}\text{Sb}_4\text{S}_{13}$	Fe1	0.13(1)	0.53(1)	-	-	7(1)
	Fe2	0.36(1)*	0.22(1)*	-	-	26(1)
	Fe3	0.57(1)**	2.57(2)**	-	-	15(1)
	<i>Relaxation</i>	$\delta_{\text{Fe(III)}}^*$ $\delta_{\text{Fe(III)}}^{**}$	$\Delta_{\text{Fe(III)}}^*$ $\Delta_{\text{Fe(II)}}^{**}$	3.03(8)	1.12(4)	52(2)
$\text{Cu}_{10}\text{Fe}_2\text{Sb}_4\text{S}_{13}$	Fe1	0.14(3)	0.56(1)	-	-	7(2)
	Fe2	0.39(2)	0.23(1)	-	-	7(1)
	Fe3	0.60(2)	2.82(2)	-	-	54(1)
	<i>Relaxation</i>	$\delta_{\text{Fe(III)}}^*$ $\delta_{\text{Fe(III)}}^{**}$	$\Delta_{\text{Fe(III)}}^*$ $\Delta_{\text{Fe(II)}}^{**}$	5.64(6)	2.63(2)	32(2)

(*), (**) values of the relevant parameters were assumed to be equal to each other.

Table 6. Parameters of the ^{57}Fe Mössbauer spectra for $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$ ($x = 1.5, 2.0$) at 77 K

Sample	Subspectrum	δ [mm/s]	Δ [mm/s]	W [mm/s]	I [%]
$\text{Cu}_{10.5}\text{Fe}_{1.5}\text{Sb}_4\text{S}_{13}$	Fe1	0.25(2)	0.91(2)	0.29*	9(3)
	Fe2	0.44(1)	0.27(1)	0.29(1)*	51(3)
	Fe3	0.72(2)	2.92(2)	0.29*	40(1)
$\text{Cu}_{10}\text{Fe}_2\text{Sb}_4\text{S}_{13}$	Fe1	0.25(3)	0.91(1)	0.27*	7(2)
	Fe2	0.43(1)	0.21(2)	0.35(4)	17(2)
	Fe3	0.73(2)	3.04(2)	0.27(2)*	76(1)

(*) values of the relevant parameters were assumed to be equal to each other.

Figure Captions

Figure 1. Unit cell parameter a (Å) as a function of Fe content in $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$. Note that the size of the error bar is smaller than the size of the circle representing the unit cell value.

Figure 2. Crystal structure of $\text{Cu}_{11.0}\text{Fe}_{1.0}\text{Sb}_4\text{S}_{13}$.

Figure 3. Variants of Cu2-Sb contacts (shown in orange) in the crystal structure of $\text{Cu}_{11.0}\text{Fe}_{1.0}\text{Sb}_4\text{S}_{13}$. The central part shows close-lying split Cu2 atoms. Labels under the figures are the numbers of the Sb-Cu2 bonds for each Sb atom in a cluster.

Figure 4. ^{57}Fe Mössbauer spectra for $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$ with $x = 0.8, 1.0$, and 1.2 at 300 K

Figure 5. ^{57}Fe Mössbauer spectra for $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$ with $x = 1.5$ and 2.0 at 300 K

Figure 6. ^{57}Fe Mössbauer spectra for $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$ with $x = 1.5$ and 2.0 at 77 K

Figure 7. Electron exchange scheme. U_0 is a potential well difference and E_A is the intervening potential barrier. See text for explanations.

Figure 8. Inverse magnetic susceptibility ($1/\chi$) versus temperature (T) at 5 T external field for $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$ with $x = 0.8, 1.0, 1.2$, and 1.5 .

Figure1

Figure2

Figure3

Figure4

Figure5

Figure6

Figure7

Figure8

Synthetic iron-containing tetrahedrites, $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$, display a variable valence state and role of iron. At low iron content two nonequivalent and non-interacting Fe^{3+} cations occur. At higher levels of substitution, room-temperature Mössbauer spectra indicate the electron hopping between part of Fe^{3+} and Fe^{2+} centers, which freezes out upon cooling down to 77 K, whereas the rest of iron atoms exists as valence-localized Fe^{3+} and Fe^{2+} cations.