Mössbauer study of isomorphous substitutions in 
Cu$_2$Fe$_{1-x}$Cu$_x$SnS$_4$ and Cu$_2$Fe$_{1-x}$Zn$_x$SnS$_4$ series

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Abstract. The investigation of isomorphous substitutions in minerals of stannite group was carried out for two series Cu$_2$FeSnS$_4$ – Cu$_3$SnS$_4$ (stannite – kuramite) and Cu$_2$FeSnS$_4$ – Cu$_2$ZnSnS$_4$ (stannite – kesterite) by $^{57}$Fe and $^{119}$Sn Mössbauer spectroscopy. The calculation of the lattice contribution to the electric field gradient tensor at the $^{57}$Fe nuclei and an estimation of the quadrupole shift for the determination of Fe$^{3+}$ atom positions in the structure were carried out. The charge and structural states of Fe and Sn atoms in compounds of the two systems were determined. The schemes of isomorphous substitutions were found for both series in all range of iron concentrations. The changes in the covalence degree of the bonds Fe$^{2+}$ – S, Fe$^{3+}$ – S and Sn$^{4+}$ – S in the process of the substitution were found.

1. Introduction

The compounds of stannite group (Cu$_2$FeSnS$_4$) are important among natural and synthetic sulfides. The interest to study sulfide minerals is generated by their wide abundance in nature. Many isomorphous elements are typical for minerals of the stannite family. The most known is Fe in kuramite (Cu$_3$SnS$_4$) and kesterite (Cu$_2$ZnSnS$_4$). Stannite and kesterite have newly attracted attention as possible photovoltaic materials. The compounds of stannite family are the fine objects for the solution of different crystal chemistry problems. The knowledge about details of sulfide structure is necessary for development of modern technology of natural raw material processing.

Mössbauer spectroscopy is the powerful and effective method, which allows one to determine the valence state and atom coordination in a structure. Therefore these two isomorphous series Cu$_2$FeSnS$_4$ – Cu$_3$SnS$_4$ (stannite – kuramite) and Cu$_2$FeSnS$_4$ – Cu$_2$ZnFeSnS$_4$ (stannite – kesterite) have been studied by $^{57}$Fe and $^{119}$Sn Mössbauer spectroscopy.

2. Objects and methods

Synthesis of the series Cu$_2$Fe$_{1-x}$Cu$_x$SnS$_4$ was carried out using standard techniques described in [1]. The synthesis of compounds of the series Cu$_2$Fe$_{1-x}$Zn$_x$SnS$_4$ was described in [2]. Three-stage process

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of re-ordering of the Cu\(^{+}\), Zn\(^{2+}\) and Fe\(^{2+}\) cations among tetrahedral positions of the structure under Fe\(^{2+}\) ↔ Zn\(^{2+}\) substitution using simultaneous Rietveld analysis of X-ray and neutron powder diffraction data were found [2].

Mössbauer investigations of all samples were carried out at room temperature with the spectrometer operated in constant acceleration mode and equipped with \(^{57}\)Co and \(^{119}\)Sn sources. Mössbauer spectra were processed by model fitting (for \(^{57}\)Fe Mössbauer spectra) and extracting hyperfine parameter distributions (for \(^{119}\)Sn Mössbauer spectra). The isomer shifts values are reported relative to \(\alpha\)-Fe and BaSnO\(_3\) for \(^{57}\)Fe and \(^{119}\)Sn Mössbauer spectra accordingly. The lattice contribution to the electric field gradient tensor at the \(^{57}\)Fe nuclei was calculated for Fe\(^{3+}\) cations using the formal point charge model to estimate the quadrupole shifts of the Mössbauer spectrum components. The programs SPECTR, DISTRI and LATTICE from MSTools Complex were used [3].

3. Results and discussion

\(^{57}\)Fe Mössbauer spectra for the samples of series Cu\(_2\)Fe\(_{1-x}\)Cu\(_x\)SnS\(_4\) are shown in figure 1. It was found that below the boundary concentration \(x_0 \approx 0.5\) well-resolved quadrupole doublet corresponding to Fe\(^{2+}\) atoms and poorly resolved quadrupole doublet corresponding to Fe\(^{3+}\) atoms were observed in the spectra. The relative intensity of the second doublet rapidly increases with increase in \(x\) [1, 4]. To ensure the charge balance the increase in Fe\(^{3+}\) concentration should be accompanied with the increase in Cu\(^{1+}\) ions. The isomorphous substitution is realized in this range \(0 \leq x \leq x_0\) by the scheme 2Fe\(^{2+}\) → Cu\(^{1+}\) + Fe\(^{3+}\) and the formula of compounds is the following Cu\(_{1+x}\)Fe\(_{1-x}\)Sn\(^{4+}\)S\(_4^2\). When \(x\) exceeds \(x_0\) the quadrupole doublet corresponding to Fe\(^{3+}\) atoms disappears in the spectra. This allows to propose for this range \(x_0 \leq x \leq 1\) the following scheme of isomorphous substitution Cu\(^{1+}\) + Fe\(^{3+}\) → 2Cu\(^{2+}\) and corresponding formula is Cu\(_{1-x}\)Fe\(_{2x}\)Sn\(^{4+}\)S\(_4^2\).

\(^{57}\)Fe Mössbauer spectra for all compounds of series Cu\(_2\)Fe\(_{1-x}\)Zn\(_x\)SnS\(_4\) are a superposition of two quadrupole doublets corresponding to Fe\(^{2+}\) and Fe\(^{3+}\) atoms (figure 2). The analysis of spectra showed that about 90% of iron atoms were divalent. The relative intensities of subspectra corresponding to Fe\(^{2+}\) and Fe\(^{3+}\) atoms remain virtually constant for all range of Zn concentrations in contrast to the data of [5]. It could be caused by the synthesis conditions.

Figure 1. Typical \(^{57}\)Fe Mössbauer spectra of Cu\(_2\)Fe\(_{1-x}\)Cu\(_x\)SnS\(_4\) compounds for \(x = 0.1, x = 0.3\) and \(x = 0.7\).

Figure 2. Typical \(^{57}\)Fe Mössbauer spectra of Cu\(_2\)Fe\(_{1-x}\)Zn\(_x\)SnS\(_4\) compounds for \(x = 0.1, x = 0.3\) and \(x = 0.7\).

\(^{119}\)Sn Mössbauer spectra of both series are poorly resolved paramagnetic type spectra. More intensive doublet with the parameters \(\delta \approx 1.5\) mm/s and \(\epsilon \approx 0.15\) - 0.35 mm/s is related to tin atoms for strong covalent bonds Sn\(^{4+}\) - S. Small amount of SnO\(_2\) are presented in all samples.
The dependencies of hyperfine parameters of $^{57}$Fe and $^{119}$Sn Mössbauer spectra on $x$ for both series are shown in figures 3 and 4. The average isomer shift $\delta_{\text{mid}}$ corresponding to Fe$^{3+}$ ions increases in both series with an increase in $x$ (figure 3a). This behavior of the isomer shift for the nuclei $^{57}$Fe corresponds to a decrease in charge density of electrons at nucleus by decreasing the effective number of 4s-electrons. Hence the covalence degree of the bonds Fe$^{3+}$ - S increases with an increase in iron atom concentration. Observed increase in $\delta_{\text{mid}}$ for Fe$^{3+}$ in Cu$_2$Fe$_{1-x}$Cu$_x$SnS$_4$ corresponds to a decrease in the covalence degree of Fe$^{3+}$ - S bonds with increasing iron concentration. A small decrease in $\varepsilon_{\text{mid}}$ for Fe$^{3+}$ under Fe substitution by Cu in Cu$_2$Fe$_{1-x}$Cu$_x$SnS$_4$ (figure 3b) can be attributed to a slight decrease in the distortion degree of local symmetry of Fe atoms. For Fe$^{2+}$ ions in Cu$_2$Fe$_{1-x}$Cu$_x$SnS$_4$ the average quadrupole shift $\varepsilon_{\text{mid}}$ rapidly decreases with an increase in $x$. This behavior can be explained by a decrease in number of Jahn-Teller ions Fe$^{3+}$, which cause a distortion of local structures along the axis 4 of local symmetry. The average values $\delta_{\text{mid}}$ and $\varepsilon_{\text{mid}}$ for Fe$^{2+}$ atoms in Cu$_2$Fe$_{1-x}$Zn$_x$SnS$_4$ virtually do not change with increase in Zn concentration (figure 3). This behavior is due to the isovalent substitution Fe$^{2+}$(T$_d$) $\rightarrow$ Zn$^{2+}$(T$_d$) and the small difference between the radii of the cations Zn$^{2+}$ and Fe$^{2+}$. Thus, the covalence degree of Fe$^{2+}$ – S bond does not change with increasing $x$.

The values of isomer shift of subspectra corresponding to Fe$^{2+}$ ions are typical for Fe$^{2+}$ ions in the tetrahedral environment of sulfur atoms [6]. The values of $\delta$ for subspectra corresponding to ions Fe$^{3+}$ are more typical for octahedral surrounding of Fe$^{3+}$ cations than tetrahedral one [6]. Therefore, it was previously suggested that the Fe$^{3+}$ atoms occupied the octahedral positions 8g formed by sulfur atoms [1, 4]. The best value of R-factor during the structure refinement by Rietveld method was obtained for...
some compounds of series Cu$_{3-x}$Fe$_x$SnS$_4$ based on this assumption [1]. However new data of XAFS analysis showed that iron atoms occupied only tetrahedral sites in the structure [7].

To determine what type of structural positions are occupied by Fe$^{3+}$ atoms in the structure of Cu$_2$Fe$_{1-x}$Cu$_x$SnS$_4$ compounds we have calculated the lattice contribution to the electric field gradient tensor at the $^{57}$Fe nuclei using the formal point charge model. The bond valences of Sn atoms in different structure positions were calculated using the known values of bond lengths [8]. These calculated bond valence values for all positions except b-positions significantly exceed 4+. The quadrupole shifts for Fe$^{3+}$ cations in the compounds with a low concentration of iron atoms for different cations distribution among nonequivalent 2a, 2c and 2d- crystallographic positions of the structure were estimated. The average experimental value of quadrupole shift is close to $\varepsilon$ for Fe$^{3+}$ atoms in tetrahedral site (especially for 2d-) but substantially less than $\varepsilon$ for Fe$^{3+}$ atoms in octahedral 8g-site. Therefore the copper atoms replaces Fe$^{3+}$ atoms in sulfur tetrahedra seems be preferable, and more likely there are the 2d-positions. Thus the isomorphous substitution in Cu$_2$Fe$_{1-x}$CuxSnS$_4$ is realized by the two schemes: $2$Fe$^{2+}$(Td) $\rightarrow$ Cu$^{1+}$(Td)+Fe$^{3+}$(Td) for $0 \leq x \leq x_0$, and Cu$^{1+}$(Td)+Fe$^{3+}$(Td) $\rightarrow$ $2$Cu$^{2+}$(Td) in the range $x_0 \leq x \leq 1$.

The observed increase in the $^{119}$Sn isomer shift in Cu$_2$Fe$_{1-x}$Cu$_x$SnS$_4$ series (figure 4a) under the substitution of Fe atoms for Cu atoms corresponds to an increase in the charge electron density at nucleus due to increasing the effective number of 5s-electrons. Thus, the degree of covalent bond Sn$^{4+}$–S increases with the iron concentration decrease. In case of Cu$_2$Fe$_{1-x}$Zn$_x$SnS$_4$ compounds a decrease in the covalence degree of bond Sn$^{4+}$–S is observed with the increase in Zn concentration. We estimated the effective charge of Sn atoms using the dependence $\delta(x)$: $Q_{\text{Sn}} = 3.32\pm0.11$ for Cu$_2$Fe$_{1-x}$Cu$_x$SnS$_4$ and $Q_{\text{Sn}} = 3.35\pm0.11$ for Cu$_2$Fe$_{1-x}$Zn$_x$SnS$_4$ series. The increase in quadrupole shift $\varepsilon$ for the $^{119}$Sn subspectrum is observed with the increase in Cu concentration in case of Cu$_2$Fe$_{1-x}$Cu$_x$SnS$_4$ series and Zn concentration in case of Cu$_2$Fe$_{1-x}$Zn$_x$SnS$_4$ series (figure 4b) indicating an increase in the distortion of tetrahedrons with Sn atoms in their centers.

It should be noted that our results did not reveal the three-stage process of cation re-ordering among tetrahedral positions of the structure for Cu$_2$Fe$_{1-x}$Zn$_x$SnS$_4$ series found in [2]. This is apparently due to the fact that such re-ordering process of cations does not change the number of Cu$^{+}$, Fe$^{2+}$ and Zn$^{2+}$ atoms in the second coordination sphere for $^{119}$Sn and $^{57}$Fe atoms and hence does not lead to a noticeable changes in the hyperfine parameters of Mössbauer spectra.

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