

Fe IN FAHLERZ

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Minerals of “Fahlerz” group are the most “mystery” ore minerals with the general formula $M(I)_6M(II)_6(X,Y)_4Z_{13}$, where $M(I) = Cu, Fe, Zn, Mn, Cd, Hg$; $M(II) = Cu, Ag$; $X = Sb, As, Bi, Te$; Y and $Z = S, Se$. Despite of the long study history the structure and the peculiarities of the isomorphous replacements in the fahlerz structure remain unclear. The principal minerals of this family are tennantite, $Cu_{12}As_4S_{13}$, and tetrahedrite, $Cu_{12}Sb_4S_{13}$. Both could contain up to some iron (up to 2 f.u.).

The question of Fe valence and coordination in fahlerz was discussed in the literature more than once, but there is no unanimous opinion. According to P.Peterson and I.Miller [1] Fe occupies in tetrahedrite the positions with the coordination “3” (triangle) like Ag. N.Jonson and oth. [2], as well as E.Makovicky and S.Karup-Møller [3] suppose that Fe atoms occupy the tetrahedral positions in the structure.

For clarify the question of valence state and coordination of Fe atoms in the structure of tetrahedrites poor in Fe the pilot study of natural and synthetic tetrahedrites of various composition (Table 1) have been carried out using the Mössbauer spectroscopy (MS1001E; ⁵⁷Co in Rh; program complex MSTools).

Table 1

Sample	Formula
t-1611 (synth.)	$Cu_{10.28}Ag_{0.06}Fe_{0.87}Zn_{0.88}Hg_{0.05}Sb_{2.00}As_{1.98}S_{13}$
t-1609 (synth.)	$Cu_{10.07}Ag_{0.08}Fe_{0.68}Zn_{1.07}Hg_{0.07}Sb_{2.29}As_{1.58}S_{13}$
“Tetrahedrite”	$Cu_{6.67}Ag_{3.60}Fe_{1.68}Zn_{0.16}Sb_{4.10}As_{<0.01}S_{13}$
“B-20”	Ag and Fe content < than in “Tetrahedrite”

The main feature of four Mössbauer ⁵⁷Fe spectra is the presence of two quadrupol dublets (Fig.1, 2). The first one is well pronounced, and is remarkable for the large quadrupol shift. This characterizes the ions Fe^{2+} in S tetrahedra. The similar dublet has been obtained for stannite during the study of the isomorphous series kuramite - stannite [4]. The weakly pronounced second dublet is characterized by more large lines and could be identified as belonging to Fe^{3+} in octahedral coordination.

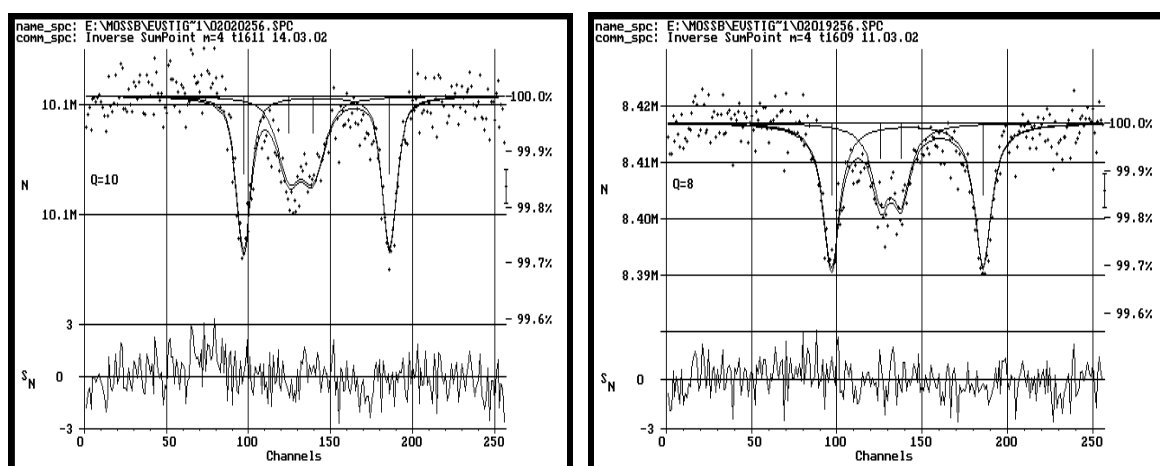


Fig.1. Mössbauer spectra of synthetic samples “t-1611” (left) and “t-1609” (right) In spite of the similarity the Mössbauer spectra of two synthetic samples (Fig.1) differ from the spectra of minerals (Fig.2). The dublet of Fe^{3+} in octahedral coordination is better pronounced in spectra of synthetic samples in comparison with the natural ones. Unlike to the Mössbauer spectra of synthetic tetrahedrites and of “B-20” that proves the position of Fe^{3+} in sulphur octahedra, the quadrupole shift in “Tetrahedrite” spectra is a little larger that is more typical for Fe^{3+} in oxygen octahedra.

The analysis of spectra obtained permits not only to determine the main parameters of ultrafine Mössbauer spectra structure, such as isomeric shift, δ , quadrupole shift, ϵ , etc, but to calculate also the intensity of Fe^{2+} and Fe^{3+} lines, that characterize the relative quantities of these ions in compounds studied (Table 2). It was shown that the direct correlation between the total Fe content and $I_{\text{Fe}^{3+}}$ is observed only for synthetic samples. For explain this observation it is not possible to ignore the role of composition. First, the natural tetrahedrites are enriched in many element admixtures. Second, the synthetic tetrahedrites are the intermediate members of the series tetrahedrite-tennantite with Sb: As~1:1, but the natural tetrahedrites studied do not contain any As.

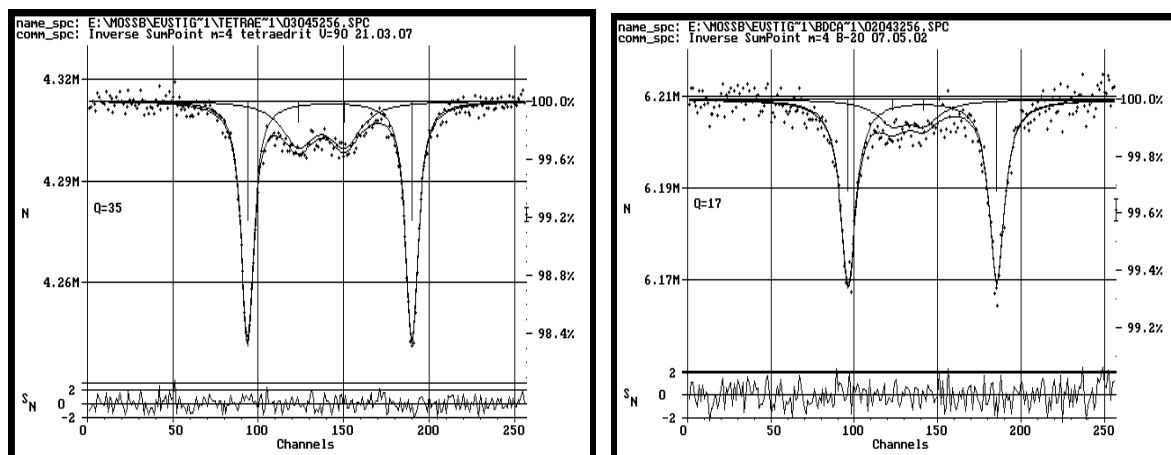


Fig.2. Mössbauer spectra of natural minerals: “Tetrahedrite” (left) and “B-20” (right)

The data obtained correspond well to the results of Mössbauer study of the stannite family compounds, kesterite and kuramite. It was shown that poor in Fe varieties of these phases contain Fe^{3+} in octahedral coordination [4,5]. Possibly the isomorphous replacement Cu-Fe in fahlerz is carried out also according to the complex schema depending on the total composition with the change of Fe valence.

Table 2.

Sample			$\delta, \text{mm/s}$	$\epsilon, \text{mm/s}$	$\Gamma, \text{mm/s}$	I, %
t-1611	Fe^{3+}	O_h	0.34 ± 0.03	0.22 ± 0.03	0.49 ± 0.06	43 ± 5
	Fe^{2+}	T_d	0.62 ± 0.01	1.30 ± 0.01	0.31 ± 0.02	57 ± 4
t-1609	Fe^{3+}	O_h	0.33 ± 0.02	0.18 ± 0.02	0.38 ± 0.05	35 ± 4
	Fe^{2+}	T_d	0.61 ± 0.01	1.30 ± 0.01	0.34 ± 0.03	65 ± 5
B-20	Fe^{3+}	O_h	0.35 ± 0.05	0.28 ± 0.04	0.65 ± 0.20	20 ± 5
	Fe^{2+}	T_d	0.60 ± 0.01	1.30 ± 0.01	0.32 ± 0.02	80 ± 3
“Tetrahedrite”	Fe^{3+}	O_h	0.47 ± 0.02	0.40 ± 0.02	0.66 ± 0.05	31 ± 2
	Fe^{2+}	T_d	0.61 ± 0.01	1.41 ± 0.01	0.26 ± 0.02	69 ± 2

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